Lithogeochemical and Sm-Nd and U-Pb isotope data from the Silurian–Lower Devonian Arisaig Group clastic rocks, Avalon terrane, Nova Scotia: A record of terrane accretion in the Appalachian-Caledonide orogen

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ABSTRACT

The Silurian–Lower Devonian Arisaig Group, in the Avalon terrane of Nova Scotia, consists of a thick (~1900 m) sequence of unmetamorphosed fossiliferous siliciclastic strata deposited during terrane accretionary events in the Appalachian-Caledonide orogen. Geochemistry and Sm-Nd and U-Pb (detrital zircon) isotope data of Arisaig Group rocks contrast with the underlying Avalonian rocks, indicating that they were not derived from Avalonian basement. All sedimentary rocks are characterized by strongly negative $\varepsilon_{Nd(t)}$ values (from –4.8 to –9.3, t = 430 Ma) and T_{DM} ages older than 1.5 Ga; the overall trend from the base to the top of the group is toward increasingly negative ε_{Nd} values. The fact that some Silurian sedimentary rocks contain detrital zircons of similar age suggests that basin formation was broadly coeval with active volcanism in the orogen. These samples also contain abundant Neoproterozoic–Early Cambrian zircons (ca. 620–520 Ma) and lesser abundances at ca. 1200–900 and 2200–1500 Ma. Archean zircons are very minor. The sample of Lower Devonian strata contains Late Silurian and Early Ordovician zircons and, in comparison to the Silurian samples, less abundant Cambrian (ca. 520–510 Ma) and Neoproterozoic (610–550 Ma; 834 Ma) zircons and subordinate Mesoproterozoic (1000–1200 Ma), Mesoproterozoic (1400–1600 Ma), and Paleoproterozoic (2000–2100 Ma) zircons. There are no Archean zircons. A comparison between the U-Pb detrital-zircon data and the age of tectonothermal events in potential source areas, together with regional geologic data, suggests that Silurian strata of the Arisaig Group were primarily derived from Baltica, but that there was increasing input from Laurentia by the time of deposition of the Lower Devonian strata of the group. The Arisaig Group is interpreted to have been deposited adjacent to the trailing edge of Avalonia during Appalachian accretionary events, and the geochemical and isotopic characteristics of its strata clearly record the signatures of these regional tectonic events.

Keywords: Arisaig Group, LA-ICPMS, detrital zircons, Avalon terrane, accretion, Appalachian orogen.

INTRODUCTION

The Appalachian-Caledonide orogen was formed by the accretion of suspect terranes to Laurentia-Baltica at various times during the Paleozoic followed by terminal collision with Gondwana and the formation of Pangea (Williams and Hatcher, 1983; Keppie, 1985; van Staal et al., 1998). Determining the timing and geometry of accretion of these terranes is fundamental to the understanding of the development of the orogen.

Avalonia is the largest suspect terrane in the northern Appalachian orogen. It occupies much of the southern flank of the Appalachians and also occurs in the basement rocks of Ireland, southern Britain, and adjacent parts of continental Europe (Fig. 1). Lithologic data (O'Brien et al., 1983, 1996), paleomagnetic data (Johnson and Van der Voo, 1986; Van der Voo, 1988), and faunal evidence (Pickering et al., 1988; Cocks and Fortey, 1990; Landing, 1996; Fortey and Cocks, 2003; Cocks and Torsvik, 2002) indicate that Avalonia was located along the periphery of Gondwana from the late Neoproterozoic to the Early Ordovician. Separation between Avalonia and Gondwana gradually increased during the Ordovician. Conversely, paleolatitudinal separation of Avalonia from Baltica and Laurentia disappeared by the Late Ordovician or Early Silurian (Miller and Kent, 1988; Van der Voo, 1988; McKerrow and Scotese, 1990; McKerrow et al., 1991; Soper and Woodcock, 1990; Trench and Torsvik, 1992; Potts et al., 1993; Dalziel et al., 1994; Golonka et al., 1994; Mac Niocaill and Smethurst, 1994; Hodych and Buchan, 1998; Mac Niocaill et al., 1997; Torsvik, and Rehnström, 2003). Paleontological evidence supports faunal linkages of Avalonia with Baltica by the Late Ordovician (e.g., Williams et al., 1995; Fortey and Cocks, 2003), whereas paleomagnetic data suggest that any paleolatitudinal separation between Avalonia and Laurentia had disappeared by the Early Silurian (Miller and Kent, 1988; Trench and Torsvik, 1992; Potts et al., 1993).

The nature and timing of the accretion of Avalonia to Laurentia-Baltica are fundamental to the understanding of the evolution of the Appalachian-Caledonide orogen and to the evolution of the Iapetus and Rheic Oceans that lay between Laurentia and Gondwana. However, as noted by Soper and Woodcock (1990), the available paleomagnetic and faunal data do not have the precision to identify the time of docking of Avalonia with Laurentia or Baltica. In addition, terrane boundaries have complex evolutions and are subject to postaccretionary movements that mask earlier histories. Another approach to constraining the docking of terranes is the identification of sedimentary strata that overstep the

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terrane boundary. Murphy et al. (1995, 1996a) presented geochemical and whole-rock Sm-Nd isotope data for lower Llandoverian clastic rocks from the basal formation in the Arisaig Group in the Avalon terrane of Nova Scotia, Canada. Although deposited on the Avalon terrane, the clastic rocks display no evidence of a significant contribution from underlying Avalonian basement, which suggests that these clastic rocks represent a postcollisional overstep sequence. However, the provenance of these rocks is unclear. Furthermore, there are no comparable data available from the overlying formations in the Arisaig Group.

In this paper, we provide lithogeochemical data and Sm-Nd and U-Pb detrital-zircon data for representative samples from the clastic rocks of the Lower Silurian–Lower Devonian Arisaig Group and then assess their provenance and regional tectonic setting. Deposition of the group spans much of the critical time interval during which accretion of several terranes, including Avalonia, occurred along the Laurentia-Baltica margin.

GEOLOGIC SETTING

The Avalon terrane in Atlantic Canada exposes vestiges of Neoproterozoic (ca. 760–660 Ma) arc-backarc complexes, followed by voluminous ca. 630–590 Ma arc-related volcanic and sedimentary successions, cogenetic plutons, and ca. 590–540 Ma intracontinental bimodal volcanic rocks and interlayered clastic sedimentary rocks, conformably to unconformably overlain by a Cambrian platform sequence that contains Acado-Baltic (Avalonian) fauna (e.g., Fig. 2) (Keppie, 1985; Murphy and Nance, 1989, 1991; Nance et al., 1991, 2002; Keppie et al., 2003).

The Arisaig Group occurs along the flanks of the Antigonish Highlands in the Avalon terrane of northern mainland Nova Scotia (Fig. 3A). The highlands are predominantly underlain by Neoproterozoic (ca. 618–608 Ma) arc-related volcanic and sedimentary rocks of the Georgeville Group that are a local representation of the ca. 630–540 Ma Avalonian orogenic cycle. These rocks are overlain by a Cambrian–Lower Ordovician sequence of bimodal intracontinental volcanic rocks and terrestrial to shallow-marine clastic rocks and limestones that contain typically Avalonian Acado-Baltic fauna (e.g., Landing and Murphy, 1991), implying an affinity with the northern Gondwanan margin.

Cambrian–Lower Ordovician rocks are unconformably overlain by ~80 m of bimodal intracontinental volcanic rocks and interbedded red clastic sediments, variously known as the Dunn Point Formation (north of the Hollow Fault) and the correlative Bears Brook Formation (south of the Hollow Fault, Fig. 3A). U-Pb zircon data (Hamilton and Murphy, 2004) from a rhyolite in the Dunn Point Formation yield an age of 460.0 ± 3.4 Ma. Paleomagnetic data from Dunn Point mafic rocks (Van der Voo and Johnson, 1985; Johnson and Van der Voo, 1990) imply that Avalonia was located ~10° north of Gondwana and 20° south of Laurentia at that time, implying that Avalonia had drifted from Gondwana before 460 Ma. Consideration of paleocontinental reconstructions indicates a microcontinental rifted-arc setting for Avalonia outboard from both Gondwana and Laurentia, analogous to the modern Taupo zone in northern New Zealand that separated from Australia during the Cretaceous opening of the Tasman Sea.

The Arisaig Group, described in detail by Boucot et al. (1974) and Murphy (1987), consists of an 1800–1900 m continuous stratigraphic sequence dominated by shallow-marine fossiliferous siliciclastic rocks that disconformably overlie the Dunn Point and Bears Brook Formations and contain Llandoverian to Lochkovian fossils (Fig. 3B).

The lower Llandoverian Beechill Cove Formation contains conglomerate and shale

Figure 1. (A) Map of the North Atlantic borderlands in their pre-Mesozoic drift positions showing the distribution of Avalonia and other Neoproterozoic peri-Gondwanan terranes (modified from Strachan and Taylor, 1990; Nance and Murphy, 1994). The part of Avalonia in Atlantic Canada is identified as West Avalonia; the part in Britain and Ireland is known as East Avalonia. Only peri-Gondwanan terranes where Cambrian overstep sequences occur are identified (see Theokritoff, 1979; Keppie, 1985). S. A.—South America. (B) Late Neoproterozoic reconstruction (modified from Nance et al., 2002) relative to the continental reconstruction of Dalziel (1997). For alternative reconstruction of Baltica, see Hartz and Torsvik (2002). Peri-Gondwanan terranes occur along the northern periphery of Gondwana (Ch—Chortis block, Ox—Oaxaquia, Y—Yucatán block, F—Florida).

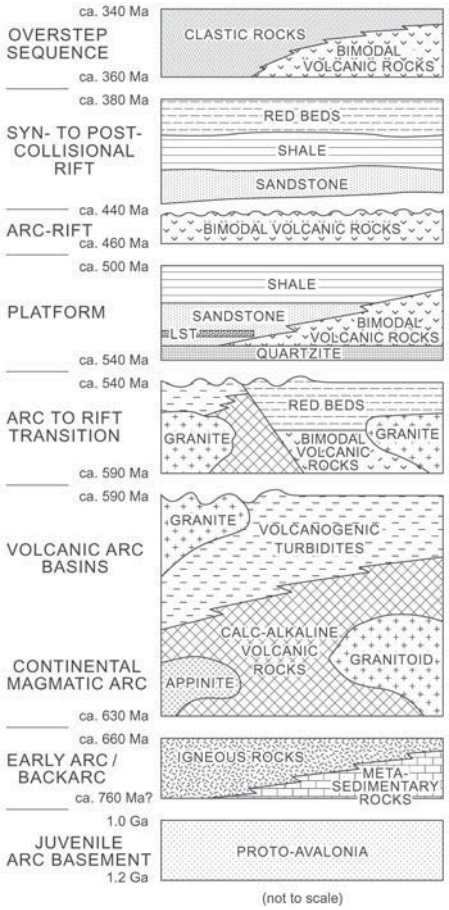

Figure 2. Tectonostratigraphy of the Antigonish Highlands (modified from Murphy et al., 1991; Murphy and Nance, 2002). The Arisaig Group is 440–380 Ma, and its depositional environment is classified as a syn- to postcollisional rift basin. LST—limestone.

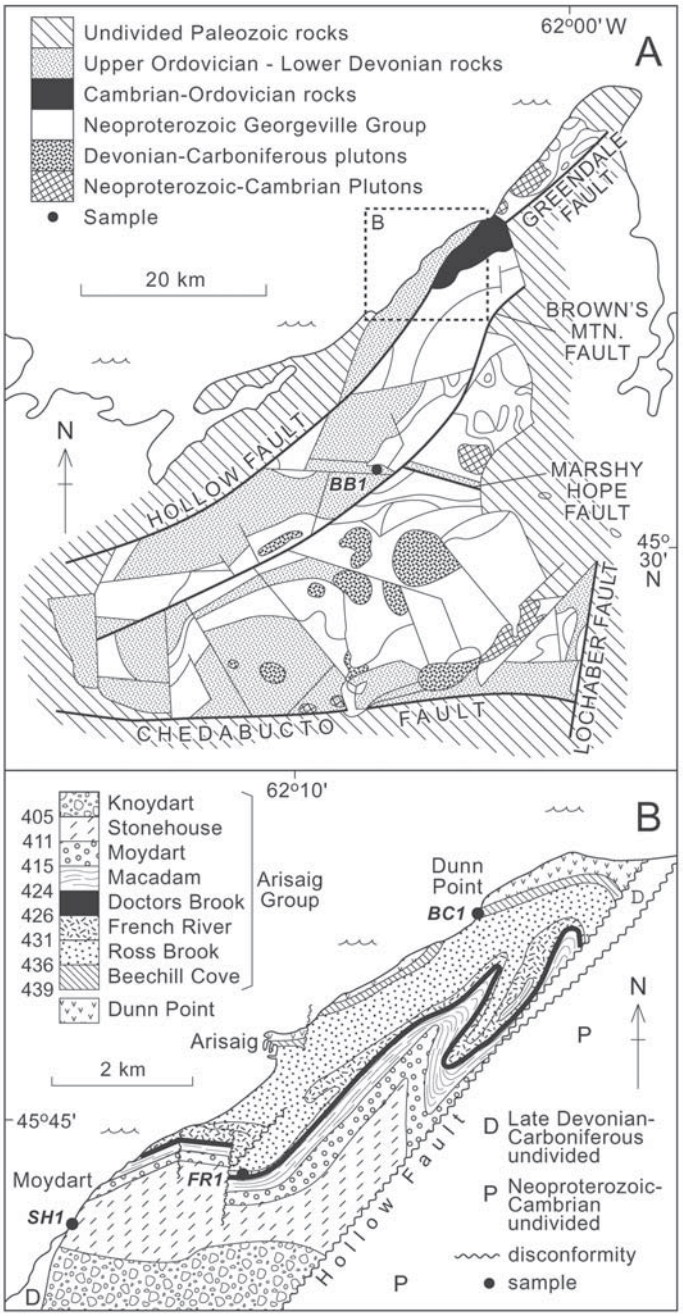

Figure 3. (A) Summary of the geology of the Antigonish Highlands. For details, see Murphy et al. (1991). (B) Summary geologic map of the Arisaig area (modified from Boucot et al., 1974). Location shown in the inset in Figure 3A. Location of samples for detrital U-Pb dating shown. Numbers in legend show the depositional age (in Ma) at the base of each formation (see Waldron et al., 1996).

deposited in a nearshore environment, followed by interbedded mudstone, shale, and sandstone (Pickerill and Hurst, 1983). The formation grades upward into the middle to upper Llandoverian Ross Brook Formation, which consists of graptolite-bearing black shale, muddy siltstone, arenaceous limestone, and ash beds (Boucot et al., 1974; Hurst and Pickerill, 1986; Bergström et al., 1997). These rocks are conformably overlain by the French River Formation, a sequence of Wenlockian interbedded green fissile shale, siltstone, and sandstone and minor ironstone followed by laminated shales, minor siltstone, and arenaceous limestone of the upper Wenlockian Doctors Brook Formation. The overlying lower Ludlovian MacAdam Brook Formation consists of interbedded fissile shale, calcareous siltstone, and fossiliferous limestone and minor ash beds and is overlain by the upper Ludlovian Moydart Formation, which consists of green interbedded siltstone, shale, mudstone, and limestone overlain by subaerial red mudstones with caliche (Dineley, 1963, Lane and Jensen, 1975; Waldron et al., 1996). These strata are conformably overlain by the Pridolian Stonehouse Formation, which consists of interbedded mudstones, shales with minor siltstones, and sandstones. The overlying Knoydart Formation consists of interbedded red and green coarse- to fine-grained clastic rocks deposited in deltaic and fluviatile environments (Boucot et al., 1974).

Waldron et al. (1996) interpreted the subsidence history of the Arisaig Group as an initial phase of rapid subsidence and extension (30% to 60%) in the early Llandoverian followed

TABLE 1. MAJOR, MINOR, AND TRACE ELEMENT ANALYSES OF CLASTIC ROCKS OF THE ROSS BROOK (RBl—LOWER; RBm—MIDDLE; RBu—UPPER), FRENCH RIVER (FR), DOCTORS BROOK (DB), AND STONEHOUSE (St) FORMATIONS OF THE ARISAIG GROUP

Sample	FK-1	FK-2	FK-3	FK-4	FK-5	FK-6	FK-7	FK-8	FK-9	FK-10	FK-11	FK-12	FK-13	FK-14	FK-15	FK-16	FK-17	FK-18	FK-19	FK-20	FK-21	FK-22	FK-23
Formation	RBl	RBl	RBm	RBm	RBu	RBu	RBu	FR	FR	FR	FR	DB	DB	DB	DB	St	St	St	St	St	St	St	St
SiO_2	59.60	70.04	60.72	67.61	63.15	69.25	65.02	75.67	76.01	11.27	11.42	71.02	69.43	66.53	65.57	73.76	69.93	55.61	72.91	52.60	59.81	71.15	56.51
TiO_2	1.19	0.92	0.75	0.74	1.14	0.83	1.11	0.66	0.63	0.34	0.31	0.97	1.03	1.07	0.70	0.69	0.67	0.57	0.64	0.54	0.67	0.77	0.2
Al_2O_3	21.19	13.06	6.10	10.85	18.80	10.46	16.87	8.51	7.88	7.81	7.63	13.98	15.42	16.69	5.00	8.88	10.26	8.47	10.49	7.73	9.31	11.88	7.70
Fe_2O_3	6.54	8.22	8.19	8.81	7.10	8.18	7.65	10.17	8.26	72.41	67.69	6.28	6.56	6.85	4.43	2.61	4.05	1.54	4.19	1.91	2.97	4.76	1.82
MnO	0.02	0.04	0.52	0.20	0.05	0.32	0.09	0.07	0.12	0.20	0.38	0.02	0.04	0.03	0.62	0.10	0.09	0.27	0.08	0.24	0.17	0.05	0.26
MgO	1.42	1.26	1.66	1.40	1.32	1.18	1.29	1.09	0.91	0.90	0.94	0.96	1.06	1.12	1.58	1.17	2.01	0.83	2.02	1.14	1.58	2.72	1.14
CaO	0.15	0.33	9.85	2.91	0.16	2.53	0.46	0.39	1.79	1.40	4.33	0.07	0.14	0.22	9.25	4.64	4.37	15.78	2.52	17.88	11.42	1.42	15.94
Na_2O	0.87	0.27	0.06	0.20	0.82	0.51	0.77	0.01	0.02	0.24	0.33	0.67	0.76	0.70	0.66	1.54	1.66	1.90	1.97	1.88	1.94	1.81	1.87
K_2O	3.86	1.90	0.73	1.53	3.47	1.63	2.97	0.95	1.02	0.09	0.03	2.59	2.88	3.20	0.92	1.54	1.65	1.50	1.74	1.07	1.48	1.91	0.99
P_2O_5	0.09	0.08	0.06	0.07	0.09	0.08	0.12	0.06	0.67	1.11	0.73	0.05	0.07	0.18	0.10	0.23	0.21	0.18	0.16	0.19	0.15	0.13	0.17
L.O.I.	5.40	3.48	11.58	5.47	4.29	5.14	4.28	2.62	2.93	3.40	6.26	2.88	3.19	3.46	10.85	4.95	5.11	12.88	3.74	14.77	10.41	3.69	13.41
Total	100.33	99.59	100.22	99.78	100.37	100.10	100.62	100.20	100.25	99.18	100.06	99.50	100.59	100.14	99.68	100.11	100.11	99.52	100.46	99.94	99.91	100.29	100.43
V	162	117	85	101	151	102	144	102	88	263	240	129	137	143	77	77	80	67	78	64	76	94	71
Cr	96	51	30	53	83	51	74	51	36	119	99	65	73	77	17	79	89	166	71	58	72	90	71
Co	26	31	24	30	29	24	28	38	31	142	131	27	26	27	8	8	15	<5	16	<5	8	20	6
Zr	207	269	595	220	252	308	260	533	466	198	180	312	323	315	629	449	328	242	142	293	356	250	336
Ba	193	251	206	354	598	350	536	93	107	<5	81	570	495	484	206	328	301	199	383	142	167	295	362
La	62	41	26	32	60	26	65	39	36	81	63	47	50	53	29	38	40	24	31	23	35	41	19
Nd	58	36	30	25	52	31	57	41	51	161	124	34	47	49	31	50	38	34	44	30	36	32	28
Ni	37	38	17	34	40	37	46	35	20	51	38	33	35	42	<3	20	97	119	37	18	17	37	16
Cu	31	30	36	37	35	32	35	33	30	57	57	26	27	29	24	<5	7	65	82	22	16	8	25
Zn	63	81	70	82	83	78	72	119	124	123	124	85	90	92	26	45	80	23	62	34	54	83	115
Ga	28	18	5	15	25	13	24	12	10	11	8	19	20	24	<5	8	11	7	12	7	8	17	7
Rb	162	82	32	63	146	68	123	44	50	<2	<2	116	125	135	50	78	78	65	82	49	66	91	48
Sr	110	59	101	74	84	52	81	43	63	83	122	65	82	89	140	127	135	389	142	463	325	69	303
Y	43	25	29	23	41	29	41	23	35	64	55	28	32	39	26	35	27	31	22	28	27	21	26
Nb	22	18	16	15	20	16	20	12	12	14	11	18	20	20	13	14	12	12	13	11	14	14	12
Pb	21	15	12	15	20	11	26	22	19	24	38	31	21	19	11	9	10	19	49	12	12	11	25
Th	17	14	10	10	17	10	16	12	11	6	5	16	16	18	14	17	14	12	11	11	16	15	12
U	3	3	5	1	3	4	3	1	2	<1	<1	2	4	2	6	4	3	3	4	3	3	5	4
La		27.08	24.25			25.29		33.08	30.69			35.79	38.56			48.49		33.08	34.17	33.50			34.14
Ce		55.12	53.06			53.16		73.70	69.99			69.93	76.59			109.81		71.19	77.49	72.90			73.36
Pr		6.50	6.37			6.57		8.41	8.50			8.09	8.90			13.44		8.71	9.68	8.98			9.16
Nd		25.28	24.78			26.03		31.94	36.58			30.37	34.56			54.59		35.45	39.14	36.36			36.67
Sm		5.19	4.87			5.68		5.89	9.52			5.77	6.69			11.74		7.01	7.55	7.18			7.16
Eu		1.13	1.16			1.32		1.19	2.28			1.14	1.34			2.22		1.47	1.51	1.51			1.55
Gd		4.66	5.50			6.05		4.92	11.41			5.10	5.84			11.40		8.04	8.00	8.08			7.92
Tb		0.74	1.01			0.96		0.81	1.68			0.86	0.94			1.74		1.26	1.23	1.26			1.24
Dy		4.60	6.70			5.95		5.23	9.35			5.56	5.98			10.37		7.67	7.29	7.64			7.52
Ho		0.95	1.42			1.19		1.09	1.61			1.09	1.15			1.86		1.36	1.25	1.36			1.32
Er		2.81	4.29			3.39		3.33	4.27			3.32	3.44			5.16		3.74	3.37	3.78			3.66
Tm		0.42	0.67			0.50		0.53	0.59			0.49	0.52			0.73		0.53	0.47	0.54			0.53
Yb		2.85	4.62			3.33		3.60	3.73			3.40	3.51			4.69		3.31	3.03	3.46			3.58
Lu		0.43	0.73			0.51		0.56	0.56			0.52	0.54			0.69		0.44	0.41	0.47			0.49
Hf		7.47	18.83			8.85		14.41	13.00			9.88	9.38			13.87		6.38	6.62	7.80			9.28
Ta		1.15	1.03			1.02		0.91	0.84			1.32	1.30			1.01		0.46	0.86	0.68			0.70
Th		10.19	11.46			9.04		12.98	9.68			12.12	12.58			14.19		8.46	9.88	9.86			9.97

Note: For Beechill Cove Formation data, see Murphy et al. (1996a). Major (wt%) and trace element (ppm) analyses were determined by X-ray fluorescence at St. Mary's University, Halifax. The precision and accuracy of these determinations are generally better than 5%, with the exception of Nb and Cr, for which precision and accuracy are generally better that 10%. Rare earth element analyses were determined by instrument neutron activation by X-Ray Assay Laboratories, McMaster University, with a precision generally between 5% and 10%. For Beechill Cove data, see Murphy et al. (1996b). LOI—loss on ignition.

TABLE 2. Sm AND Nd CONTENTS AND Nd ISOTOPE COMPOSITION OF THE ARISAIG GROUP ROCKS

Sample	Formation†	Nd (ppm)	Sm (ppm)	$^{147}Sm/^{144}Nd$	$^{143}Nd/^{144}Nd$	2σ	$\varepsilon_{Nd(t=430)}$	$\varepsilon_{Nd(t=400)}$	$\varepsilon_{Nd(t=0)}$	$T_{(DM)}$
FK-2	RBl	27.38	5.46	0.1204	0.512107	4	–6.2	–6.5	–10.4	1525
FK-3	RBm	25.00	4.80	0.1161	0.512052	4	–7.0	–7.3	–11.4	1543
FK-6	RBu	27.35	5.73	0.1267	0.512136	3	–6.0	–6.2	–9.8	1584
FK-8	FR	32.16	5.96	0.1121	0.512015	4	–7.5	–7.8	–12.2	1538
FK-9	FR	39.11	10.15	0.1569	0.512154	3	–7.3	–7.4	–9.4	2395
FK-12	DB	31.95	5.89	0.1114	0.511995	3	–7.9	–8.2	–12.5	1558
FK-13	DB	37.20	7.02	0.1141	0.512008	4	–7.8	–8.1	–12.3	1580
FK-16	St	55.51	11.79	0.1284	0.512039	4	–7.9	–8.2	–11.7	1789
FK-18	St	38.07	8.23	0.1307	0.512076	4	–7.3	–7.6	–11	1771
FK-19	St	36.89	9.92	0.1625	0.512073	4	–9.2	–9.3	–11	2943
FK-20	St	35.26	7.70	0.1320	0.512075	5	–7.4	–7.7	–11	1801
FK-23	St	35.82	7.68	0.1297	0.512024	4	–8.3	–8.6	–12	1844

Note: Chemical separations and isotopic analyses were determined at the Atlantic Universities Regional Isotopic Facility, Memorial University of Newfoundland. The $^{143}Nm/^{144}Nd$ ratios are measured by thermal-ionization mass spectrometry, after chemical separation of Nd from Sm and other REEs by ion-exchange chemistry. La Jolla Nd standard gave an average value of 0.511860. ε_{Nd} values are relative to $^{143}Nd/^{144}Nd = 0.512638$ and $^{147}Sm/^{144}Nd = 0.196593$ for present-day CHUR (chondritic uniform reservoir) (Jacobsen and Wasserburg, 1980) and $\lambda(^{147}Sm) = 6.54 \times 10^{-12}$/yr. $T_{(DM)}$ values were calculated by using the model of DePaolo (1981, 1988). ε_{Nd} values were calculated for t = 430 Ma and t = 400 Ma (which represents the range in the age of deposition of the Arisaig Group) and for the present-day (t = 0); DM—depleted mantle. The 2σ errors refer to the least significant digit.

†See Table 1 for abbreviations.

by thermal relaxation and slower subsidence rates in the Wenlockian and Ludlovian. The vastly increased rates of subsidence and accommodation-space creation in the Pridolian (as represented by the Stonehouse Formation) are attributed to loading of the Avalonian margin as a result of interaction with a neighboring terrane (Waldron et al., 1996).

ANALYTICAL METHODS

Lithogeochemistry

Twenty-one representative samples of medium-grained sandstones and siltstones were selected for major and trace element analysis: seven from the Ross Brook Formation, two from the French River Formation, four from the Doctors Brook Formation, and eight from the Stonehouse Formation. Sample locations are shown in Figure 3B, and the data are shown in Table 1. Samples from the Ross Brook, French River, and Doctors Brook Formations are remarkably uniform, generally consisting of angular to subangular quartz (~55%), ~5% plagioclase, which displays moderate alteration to sericite, ~5% detrital muscovite, and minor chlorite, clay minerals, and hematite. The Stonehouse Formation is broadly similar to the underlying formations, but also contains variable amounts of calcite in the matrix and lesser abundance of clay minerals.

Twelve samples were analyzed for REEs (rare earth elements) (Table 2): three from the Ross Brook Formation, two each from the French River and Doctors Brook Formations, and five from the Stonehouse Formation. The major and selected trace elements were analyzed by X-ray fluorescence and the REEs by neutron activation at the Nova Scotia Regional Geochemical Centre at St. Mary's University, Halifax. The accuracy and precision of all analyses are generally better than 10%. Details of the analytical methods are given in Murphy et al. (1991).

Sm-Nd Isotope Data

Ten representative samples (two from the Ross Brook Formation, two from the French River Formation, one from the Doctors Brook Formation, and five from the Stonehouse Formation) were also analyzed for Sm-Nd compositions at the Atlantic Universities Regional Isotopic Facility (AURIF) at Memorial University, Newfoundland (Table 2). Analytical procedures are described in Kerr et al. (1995) and are given in the Appendix.

Detrital-Zircon Age Determinations

Four samples of medium-grained sandstone and siltstones from the Middle Ordovician (ca. 460 Ma; Hamilton and Murphy, 2004) Bears Brook Formation (BB-1; Dunn Point equivalent), the Llandoverian Beechill Cove Formation (BC-1), the French River Formation (FR-1), and the Stonehouse Formation (SH-1) were selected for U-Pb detrital-zircon analysis by LA-ICP-MS (laser ablation inductively coupled plasma–mass spectrometry). Analytical methods are given in Jeffries et al. (2003) and are summarized in the Appendix.

A total of 156 analyses (one analysis per grain) were performed on zircons in the following samples: BB-1 (48 analyses), BC-1 (36 analyses), FR-1 (36 analyses), and SH-1 (36 analyses). Of those analyses, 40 were rejected (11 in BB-1, 8 in BC-1, 10 in FR-1, and 11 in SH-1) on the basis of the presence of features such as discordance of >15%, high common Pb detected in the U-Pb, Th-Pb, and/or Pb-Pb isotope ratio plots, elemental U-Pb fractionation or inconsistent behavior of U-Pb and Th-Pb ratios in the course of ablation. Samples BC-1, FR-1, and SH-1 contained very small amounts of zircon (less than ~30 grains per kilogram of rock), and more than 50% of the grains could not be analyzed owing to their minute size (a feature typical of many shales).

Table 3 reports U-Pb and Pb-Pb ratios and ages for the 116 selected analyses (37 in BB-1, 28 in BC-1, 26 in FR-1, and 25 in SH-1). Concordia plots and a relative probability age plot of each of the four samples studied are presented later in the paper. The ages labeled as "reported age" in Table 3 are calculated as follows: For concordant analyses (ages whose corresponding isotope ratios have a 2σ error ellipse that, to a greater or lesser extent, overlaps the concordia curve), we report concordia ages and errors as defined by Ludwig (1998). For normally discordant analyses, we report the $^{207}Pb/^{206}Pb$ age and 2σ error. In cases where the error on the $^{207}Pb/^{206}Pb$ ratio is large owing to low ^{207}Pb contents or very short collection times (very small zircons), the error reported corresponds to the upper intercept of a discordia forced through 0 Ma. For slightly reversely discordant zircons younger than ca. 900 Ma and whose $^{207}Pb/^{206}Pb$ ages have large errors owing to small amounts of ^{207}Pb, we use the more precise $^{206}Pb/^{238}U$ age and corresponding 2σ error.

RESULTS

Major and Trace Element Data

Taken together, the major and trace element abundances of the Ross Brook, French River, and Doctors Brook (RFD) samples are very similar to those of the basal Beechill Cove Formation (BC samples; data from Murphy et al., 1996a). SiO_2 ranges from ~62 to 78 wt% (all ranges calculated on a volatile-free basis), Al_2O_3 from 6 to 22 wt%, TiO_2 from 0.65 to 1.2 wt%, CaO from trace amounts to 11 wt%, Fe_2O_3 from 5 to 9 wt%. The samples contain low Na_2O (less than 0.9 wt%) and low P_2O_5 (less than 0.1 wt%), V from 77 to 162 ppm, Sr from 43 to 120 ppm, and Nb from 13 to 22 ppm. By comparison

TABLE 3. LA-ICP-MS U-Pb RESULTS

Analysis	i.s.	Isotopic ratios and 2σ (%) errors						Ages and 2σ absolute errors (Ma)						Reported age†		
number	(s)	$^{206}Pb/^{238}U$	±2σ	$^{207}Pb/^{235}U$	±2σ	$^{207}Pb/^{206}Pb$	±2σ	$^{206}Pb/^{238}U$	±2σ	$^{207}Pb/^{235}U$	±2σ	$^{207}Pb/^{206}Pb$	±2σ	Age (Ma)	±2σ	Disc. (%)
Sample BB-1																
fe04a05	25	0.0961	1.72	0.8041	3.46	0.0607	3.16	592	10	599	16	626	68	593	10	5.4
fe04a08	40	0.0962	1.42	0.8003	1.76	0.0603	1.62	592	8	597	8	614	34	595	7	3.6
fe04b06	31	0.0972	1.62	0.7949	2.26	0.0593	2.48	598	9	594	10	578	54	596	8	–3.5
fe04a06	44	0.0968	1.72	0.8118	2.54	0.0608	2.68	595	10	603	12	632	56	599	8	5.9
fe04a13	46	0.0991	1.04	0.8196	1.16	0.0600	1.28	609	6	608	5	600	26	608	5	–1.5
fe04b10	42	0.0988	1.34	0.8212	2.02	0.0603	2.08	608	8	609	9	612	46	608	7	0.7
fe04d11	38	0.0993	1.46	0.8213	1.92	0.0600	2.42	610	9	609	9	602	54	610	6	–1.3
fe04a16	56	0.0991	1.18	0.8294	1.44	0.0607	1.58	609	7	613	7	628	34	611	5	3.0
fe04d05	35	0.0994	1.90	0.8239	2.48	0.0601	1.90	611	11	610	11	606	42	611	10	–0.8
fe04c05	52	0.0995	1.74	0.8267	1.80	0.0602	1.20	612	10	612	8	610	26	612	8	–0.3
fe04c09	31	0.1002	1.80	0.8295	2.98	0.0600	2.42	616	11	613	14	604	52	615	10	–2.0
fe04b13	48	0.1001	1.10	0.8349	1.52	0.0605	1.86	615	6	616	7	620	40	616	5	0.8
fe04c11	33	0.1004	1.30	0.8326	2.18	0.0601	2.06	617	8	615	10	608	44	616	7	–1.5
fe04c14	23	0.1007	2.30	0.8339	2.76	0.0600	2.18	619	14	616	13	604	48	617	12	–2.5
fe04a15	40	0.1003	1.70	0.8467	2.72	0.0612	2.62	616	10	623	13	644	56	618	9	4.3
fe04b05	33	0.1006	1.50	0.8139	1.86	0.0587	1.86	618	9	605	8	554	40	618	9	–11.6
fe04c12	31	0.1009	1.50	0.8342	2.30	0.0600	2.34	619	9	616	11	602	50	618	8	–2.8
fe04a09	57	0.0952	1.12	0.7942	1.40	0.0605	1.02	586	6	594	6	620	22	620	22	5.5
fe04b11	36	0.1010	2.18	0.8157	3.00	0.0586	2.12	620	13	606	14	550	46	620	13	–12.7
fe04d16	44	0.1015	1.20	0.8374	2.00	0.0598	1.92	623	7	618	9	596	42	621	7	–4.5
fe04d10	40	0.1016	1.28	0.8315	2.62	0.0594	2.24	624	8	614	12	580	48	623	8	–7.6
fe04c08	31	0.1022	2.24	0.8443	2.60	0.0599	2.28	627	13	621	12	600	50	624	11	–4.5
fe04b15	57	0.1022	1.06	0.8465	1.94	0.0601	1.70	627	6	623	9	606	38	626	6	–3.5
fe04c16	42	0.1021	1.34	0.8418	2.66	0.0598	2.22	627	8	620	12	594	48	626	8	–5.6
fe04d15	48	0.1026	1.26	0.8618	1.66	0.0609	1.56	630	8	631	8	634	34	630	7	0.6
fe04c07	38	0.0978	1.22	0.8206	1.44	0.0608	1.26	602	7	608	7	632	28	632	28	4.7
fe04c13	46	0.1052	1.42	0.8809	2.22	0.0607	2.46	645	9	641	11	630	54	644	7	–2.4
fe04b16	44	0.1108	1.18	0.9204	2.26	0.0603	2.26	677	8	663	11	612	48	677	8	–10.6
fe04c10	33	0.1226	2.04	1.1007	3.50	0.0651	3.88	746	14	754	19	776	82	748	12	3.9
fe04b08	21	0.1919	1.94	2.0816	2.24	0.0787	2.58	1132	20	1143	15	1162	52	1139	14	2.6
fe04a07	33	0.1940	1.44	2.1100	1.60	0.0789	0.86	1143	15	1152	11	1168	16	1168	16	2.1
fe04d07	25	0.2025	1.12	2.2374	2.30	0.0801	2.36	1189	12	1193	16	1200	46	1190	11	0.9
fe04d12	46	0.2075	1.44	2.3214	1.90	0.0811	1.94	1215	16	1219	14	1224	38	1218	12	0.7
fe04d08	31	0.2679	1.76	3.4827	1.46	0.0943	1.12	1530	24	1523	12	1512	20	1521	10	–1.2
fe04a10	61	0.2694	1.42	3.6925	1.76	0.0994	1.14	1538	19	1570	14	1612	22	1612	22	4.6
fe04b07	52	0.2899	1.36	4.1177	1.48	0.1030	0.84	1641	20	1658	12	1678	16	1678	16	2.2
fe04b12	46	0.4779	1.72	10.8949	1.64	0.1653	0.72	2518	36	2514	15	2510	12	2512	10	–0.3
Sample BC-1																
fe03d14	40	0.0719	1.70	0.5526	3.44	0.0557	2.70	448	7	447	12	440	60	448	7	–1.8
fe03a09	36	0.0747	1.48	0.5760	1.94	0.0559	1.28	464	7	462	7	448	28	464	6	–3.6
fe03a08	40	0.0846	1.54	0.6861	1.78	0.0588	1.78	524	8	530	7	558	38	527	6	6.1
fe03b14	15	0.0848	1.98	0.6836	2.06	0.0585	2.58	525	10	529	8	546	56	527	7	3.8
fe03d15	42	0.0888	1.30	0.7042	1.70	0.0575	2.06	548	7	541	7	510	44	545	5	–7.5
fe03c16	36	0.0883	1.84	0.7230	5.08	0.0594	5.04	546	10	552	22	580	110	546	10	5.9
fe03a15	29	0.0927	1.52	0.7619	2.58	0.0596	2.72	572	8	575	11	588	58	573	7	2.7
fe03c07	17	0.0866	1.60	0.7082	2.16	0.0593	1.14	536	8	544	9	576	24	576	24	6.9
fe03c09	21	0.0959	1.34	0.7983	3.14	0.0604	3.02	590	8	596	14	616	66	591	7	4.2
fe03b11	36	0.1002	1.82	0.8307	2.24	0.0601	2.76	615	11	614	10	608	58	615	8	–1.2
fe03b13	29	0.1002	1.38	0.8297	2.30	0.0600	2.10	616	8	613	11	604	46	615	8	–2.0
fe03d16	31	0.1013	2.26	0.8248	3.28	0.0590	3.90	622	13	611	15	566	84	617	10	–9.9
fe03b07	13	0.0953	1.42	0.8120	1.58	0.0618	2.56	587	8	604	7	666	56	666	28	11.9
fe03b06	19	0.0946	2.04	0.8184	2.80	0.0627	3.08	583	11	607	13	698	66	698	17	16.5
fe03a14	40	0.1141	1.70	0.9955	2.24	0.0633	1.60	697	11	702	11	716	34	699	10	2.7
fe03d08	31	0.1560	1.48	1.5155	1.82	0.0704	0.88	935	13	937	11	940	18	937	11	0.5
fe03a12	23	0.1631	1.94	1.6290	2.46	0.0724	1.62	974	17	981	15	996	32	980	15	2.2
fe03d12	33	0.1697	1.50	1.7010	1.12	0.0727	1.12	1010	14	1009	7	1004	22	1009	7	–0.6
fe03d10	34	0.1724	1.02	1.7060	2.60	0.0717	2.12	1025	10	1011	17	978	44	1025	10	–4.8
fe03b08	29	0.2037	1.12	2.3112	1.32	0.0823	0.96	1195	12	1216	9	1252	18	1252	18	4.6
fe03a11	15	0.1956	2.10	2.2353	2.30	0.0829	0.88	1152	22	1192	16	1264	18	1264	18	8.9
fe03c05	29	0.3083	2.26	4.5692	1.72	0.1075	1.40	1732	34	1744	14	1756	24	1747	6	1.4
fe03c13	27	0.3784	1.38	6.7130	1.58	0.1286	0.72	2069	24	2074	14	2078	12	2077	12	0.4
fe03c12	35	0.3842	2.24	7.0353	2.40	0.1328	0.84	2096	40	2116	21	2134	16	2130	15	1.8
fe03b10	33	0.3759	1.62	6.9141	1.58	0.1334	0.76	2057	29	2100	14	2142	12	2142	12	4.0
fe03a13	40	0.3958	1.02	7.2657	1.22	0.1331	0.82	2150	19	2145	11	2138	14	2144	11	–0.6
fe03d13	36	0.4012	1.64	7.5327	1.72	0.1361	1.64	2175	30	2177	15	2178	28	2177	16	0.1
fe03c08	23	0.4884	1.16	12.5960	1.16	0.1870	0.98	2564	25	2650	11	2714	16	2714	16	5.5

(*continued*)

TABLE 3. LA-ICP-MS U-Pb RESULTS (*continued*)

Analysis	i.s.	Isotopic ratios and 2σ (%) errors						Ages and 2σ absolute errors (Ma)						Reported age†		
number	(s)	$^{206}Pb/^{238}U$	±2σ	$^{207}Pb/^{235}U$	±2σ	$^{207}Pb/^{206}Pb$	±2σ	$^{206}Pb/^{238}U$	±2σ	$^{207}Pb/^{235}U$	±2σ	$^{207}Pb/^{206}Pb$	±2σ	Age (Ma)	±2σ	Disc. (%)
Sample FR-1																
jn19a05	21	0.0653	1.24	0.5021	2.46	0.0558	2.36	408	5	413	8	444	54	444	28	8.1
jn19a06	42	0.0836	2.16	0.6703	3.04	0.0582	2.72	517	11	521	12	534	60	519	10	3.2
jn19a07	44	0.0860	1.50	0.6975	3.08	0.0588	2.90	532	8	537	13	558	64	533	7	4.7
jn19a10	27	0.0874	1.08	0.7120	1.68	0.0591	1.52	540	6	546	7	568	34	542	6	4.9
jn19a08	19	0.0885	1.54	0.7085	2.70	0.0580	2.10	547	8	544	11	530	46	546	8	–3.2
jn19a09	15	0.0913	3.92	0.7332	4.10	0.0582	3.92	563	21	558	18	536	84	560	17	–5.0
jn19a11	25	0.0933	2.36	0.7480	5.26	0.0581	6.46	575	13	567	23	534	142	574	13	–7.7
jn19a12	44	0.1030	1.42	0.8567	1.64	0.0603	1.38	632	9	628	8	614	28	630	7	–2.9
jn19a13	21	0.0960	1.62	0.8063	2.46	0.0609	2.04	591	9	600	11	634	44	634	44	6.8
jn19a14	21	0.0995	2.04	0.8385	1.48	0.0611	2.56	612	12	618	7	642	54	642	27	4.7
jn19a15	33	0.1197	1.78	1.0425	2.72	0.0632	2.58	729	12	725	14	712	56	727	11	–2.4
jn19a16	13	0.1241	1.02	1.1080	2.46	0.0648	2.50	754	7	757	13	766	52	755	7	1.6
jn19b05	17	0.1502	2.40	1.4570	3.48	0.0703	3.42	902	20	913	21	938	70	907	17	3.8
jn19b06	17	0.1637	1.32	1.6307	2.10	0.0722	1.64	977	12	982	13	992	34	979	11	1.5
jn19b07	23	0.1650	1.98	1.6323	2.28	0.0718	2.48	984	18	983	14	978	50	983	13	–0.6
jn19b08	29	0.1691	1.58	1.6751	1.90	0.0719	1.68	1007	15	999	12	980	34	1001	11	–2.8
jn19b09	21	0.1469	2.42	1.4747	2.30	0.0728	2.08	883	20	920	14	1008	42	1008	42	12.4
jn19b10	27	0.1999	1.86	2.1890	2.00	0.0794	1.70	1175	20	1178	14	1180	34	1177	14	0.4
jn19b11	38	0.2006	2.02	2.2559	2.58	0.0816	1.14	1178	22	1199	18	1234	24	1234	24	4.5
jn19b12	23	0.2700	1.72	3.6197	2.40	0.0972	2.40	1541	24	1554	19	1570	44	1570	44	1.8
jn19b13	23	0.3165	2.02	4.7415	1.08	0.1086	1.66	1773	31	1775	9	1776	30	1775	9	0.2
jn19b14	27	0.3204	1.46	4.9900	2.08	0.1129	1.58	1792	23	1818	18	1846	28	1846	28	2.9
jn19b15	23	0.3088	1.20	5.0259	2.42	0.1180	1.92	1735	18	1824	21	1926	34	1926	34	9.9
jn19b16	23	0.3488	1.58	5.7446	1.76	0.1194	1.54	1929	26	1938	15	1946	28	1938	15	0.9
jn19c05	23	0.3240	2.34	5.3615	3.34	0.1200	2.44	1809	37	1879	29	1956	42	1956	21	7.5
jn19c06	15	0.3793	1.98	6.7968	1.94	0.1300	1.54	2073	35	2085	17	2096	28	2087	17	1.1
Sample SH-1																
jn24a06	25	0.0653	1.50	0.5001	4.92	0.0555	4.64	408	6	412	17	434	104	410	6	6.0
jn24a07	17	0.0665	1.64	0.5116	3.42	0.0558	3.34	415	7	419	12	442	76	416	6	6.1
jn24a08	6	0.0774	2.10	0.5971	3.48	0.0559	1.44	481	10	475	13	448	32	479	9	–7.4
jn24a09	17	0.0724	2.34	0.5699	1.18	0.0571	1.76	450	10	458	4	494	38	494	38	8.9
jn24a10	12	0.0802	2.36	0.6359	4.22	0.0575	5.68	497	11	500	17	510	124	498	11	2.5
jn24a11	17	0.0834	2.14	0.6671	2.86	0.0580	2.30	516	11	519	12	528	50	517	10	2.3
jn24a12	19	0.0844	2.14	0.6702	2.60	0.0576	4.06	523	11	521	11	512	90	522	9	–2.1
jn24c09	19	0.0887	1.44	0.7398	4.10	0.0605	4.94	548	8	562	18	620	106	548	8	11.6
jn24a13	29	0.0815	2.20	0.6606	2.98	0.0588	2.54	505	11	515	12	558	56	558	56	9.5
jn24c08	23	0.0826	2.36	0.6827	2.48	0.0599	1.96	512	12	528	10	600	42	600	20	14.7
jn24a14	27	0.0975	1.76	0.8147	3.60	0.0606	3.40	600	10	605	16	624	72	601	10	3.8
jn24c07	15	0.0822	2.26	0.6830	3.62	0.0602	3.12	509	11	529	15	610	68	610	34	16.6
jn24a15	36	0.1378	1.50	1.2779	2.50	0.0672	2.66	832	12	836	14	844	56	834	10	1.4
jn24a16	61	0.1728	1.52	1.7757	1.80	0.0745	1.26	1027	14	1037	12	1054	26	1035	12	2.6
jn24b05	13	0.1979	3.28	2.1227	4.74	0.0778	3.54	1164	35	1156	33	1140	72	1159	31	–2.1
jn24b06	19	0.2015	2.14	2.2947	2.08	0.0826	0.94	1183	23	1211	15	1258	18	1258	18	6.0
jn24b07	17	0.2393	1.56	2.9796	1.96	0.0903	2.06	1383	20	1402	15	1430	38	1430	38	3.3
jn24b08	19	0.2459	1.92	3.1360	2.50	0.0925	1.16	1417	24	1442	19	1476	22	1476	22	4.0
jn24b09	31	0.2423	1.18	3.1121	0.98	0.0932	1.16	1398	15	1436	8	1490	22	1490	22	6.2
jn24b10	31	0.2571	1.96	3.3873	2.04	0.0956	1.66	1475	26	1501	16	1538	32	1538	32	4.1
jn24b11	25	0.2721	1.42	3.7096	1.72	0.0989	1.50	1552	20	1573	14	1602	28	1602	28	3.1
jn24b12	23	0.2543	1.56	3.4930	2.38	0.0996	1.32	1460	20	1526	19	1616	24	1616	24	9.7
jn24c13	10	0.2988	3.12	4.8760	2.72	0.1183	2.08	1686	46	1798	23	1930	36	1930	36	12.6
jn24b13	27	0.3632	2.14	6.5404	1.94	0.1306	0.98	1997	37	2051	17	2104	18	2104	18	5.1
jn24b14	33	0.3646	1.56	6.6123	1.98	0.1315	1.96	2004	27	2061	17	2118	34	2118	34	5.4

Note: LA-ICP-MS detrital-zircon data for (a) sample BB-1, Bear Brook Formation, (b) sample BC-1, Beechill Cove Formation, (c) FR-1, Doctors Brook Formation, and (d) SH-1, Stonehouse Formation, Antigonish Highlands, Avalon terrane of Nova Scotia. i.s.—signal interval integrated for isotope ratio and age calculation (in seconds). Disc.—discordance calculated from $^{207}Pb/^{206}Pb$ and $^{206}Pb/^{238}U$ ages (negative values: reverse discordance).

†See text for details.

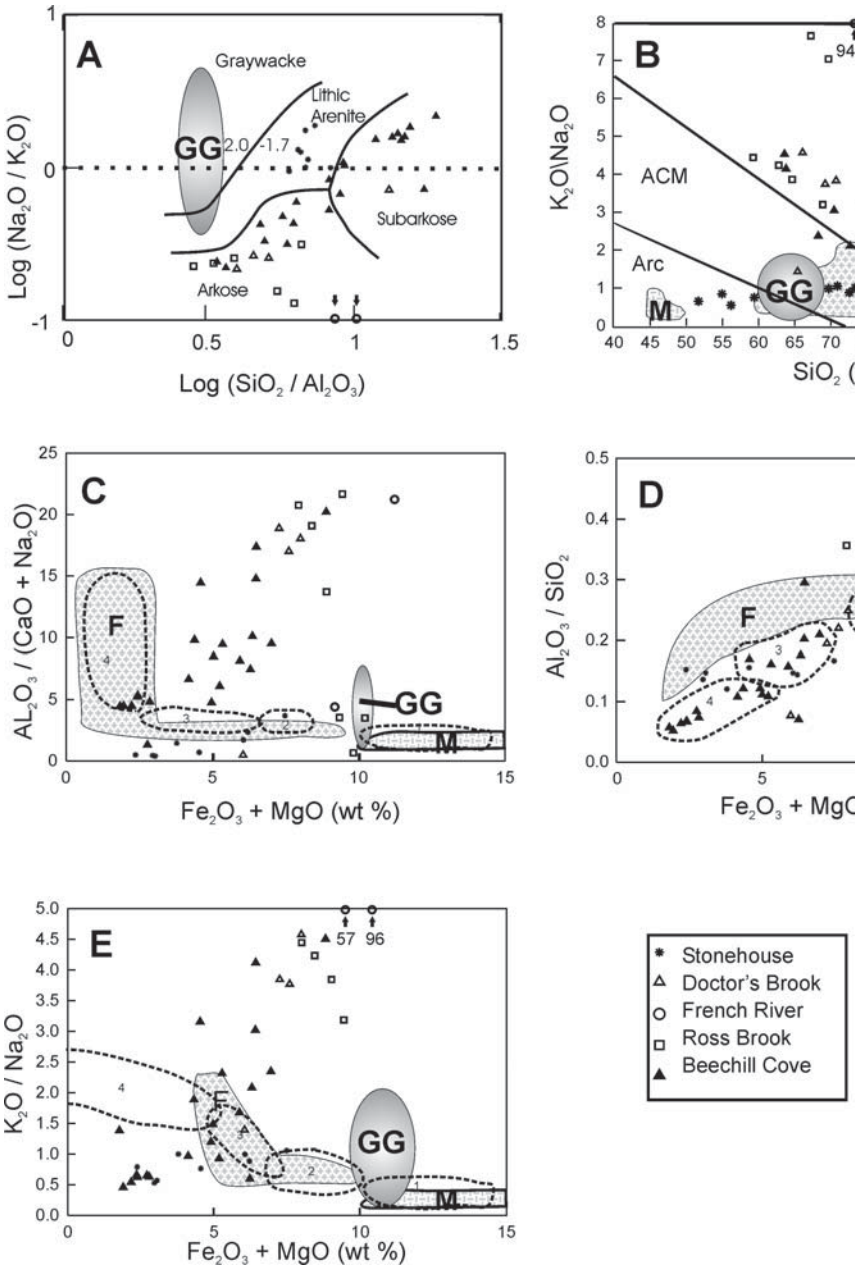

Figure 4. Arisaig Group sedimentary rocks plotted on selected published discrimination diagrams emphasizing major element chemical variations: (A) log $Na_2O + K_2O$ vs. log SiO_2/Al_2O_3; (B) K_2O/Na_2O vs. SiO_2 (after Roser and Korsch, 1986); (C) $Al_2O_3/(CaO + Na_2O)$ vs. $Fe_2O_3 + MgO$ (after Bhatia, 1983); (D) Al_2O_3/SiO_2 vs. $Fe_2O_3 + MgO$ (after Bhatia, 1983); (E) K_2O/Na_2O vs. $Fe_2O_3 + MgO$ (after Bhatia, 1983). In B, ACM—active continental margin; PM—passive margin. In C, D, and E, 1—oceanic island arc; 2—continental island arc; 3—active continental margin; 4—passive margin. GG—compositional ranges of the Neoproterozoic Georgeville Group turbidites; F—Ordovician felsic rocks; M—Ordovician mafic rocks.

with the RFD samples, the Stonehouse Formation samples (SH) have lower TiO_2 (0.55–0.8 wt%) and Fe_2O_3 (1.5–5 wt%), higher CaO (5–20 wt%), Na_2O (1.6–2.0 wt%), and P_2O_5 (0.13–0.24 wt%), lower V (67–94 ppm), higher Sr (69–463 ppm), and lower Nb (11–14 ppm).

In order to fully document the geochemistry of the Arisaig Group as a whole, Beechill Cove Formation major and trace element (12 samples) and REE data (5 samples) of the Beechill Cove are included on geochemical plots (see Murphy et al., 1996a for details). On plots such as log SiO_2/Al_2O_3 vs. log Na_2O/K_2O, most BC and RFD rocks plot on a similar linear trend, primarily reflecting variations in quartz and feldspar content. In SH samples, however, rocks with similar SiO_2/Al_2O_3 ratios have higher Na_2O/K_2O ratios than Beechill Cove or RFD rocks (Fig. 4A). On the SiO_2 vs. K_2O/Na_2O diagram, the BC and RFD analyses also show similar trends of decreasing K_2O/Na_2O ratios with increasing SiO_2 (Fig. 4B). The relatively low $Fe_2O_3 + MgO$ and Al_2O_3/SiO_2 (Figs. 4C, 4D, 4E; after Bhatia 1983) and similar K/Rb ratios of ~200 (Fig. 5) in BC, RFD, and SH are typical of upper-crustal rocks (~230; Taylor and McLennan 1985) with limited mafic components.

The apparent passive-margin to active-continental-margin signature suggested by many of the samples could equally be attributed to a source region lacking mafic rocks and/or to recycling of sediment during sediment transport. Ratios involving HFSEs (high field strength elements) and REEs are generally considered reliable indicators of provenance because they are relatively unaffected by sedimentary processes such as weathering, sorting, or diagenesis (e.g., McLennan et al., 1980; Bhatia and Crook 1986) and have low residence time in seawater (Holland, 1978). On a plot of Zr/Nb vs. Ti/Nb (Fig. 6A), Beechill Cove Formation rocks are characterized by higher Ti/Nb ratios (trend 1) relative to the overlying formations (trend 2) for similar Zr/Nb ratios. On a Zr/V vs. Ti/V plot (Fig. 6B), the Beechill Cove Formation samples

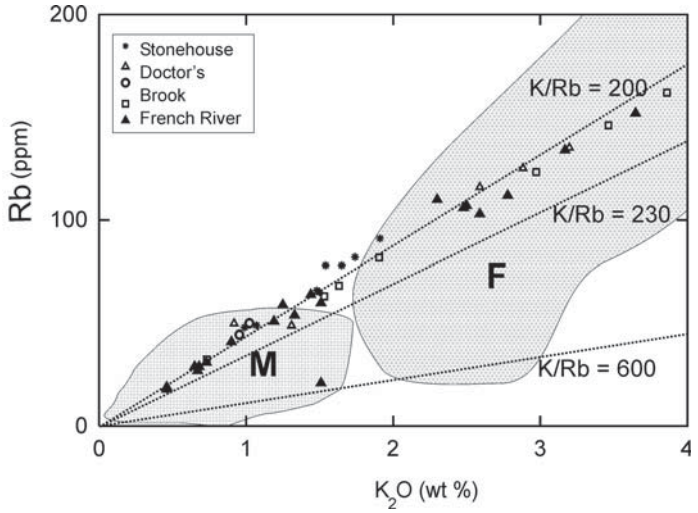

Figure 5. K/Rb ratios for the detrital rocks of the Arisaig Group. F—Ordovician felsic rocks; M—Ordovician mafic rocks.

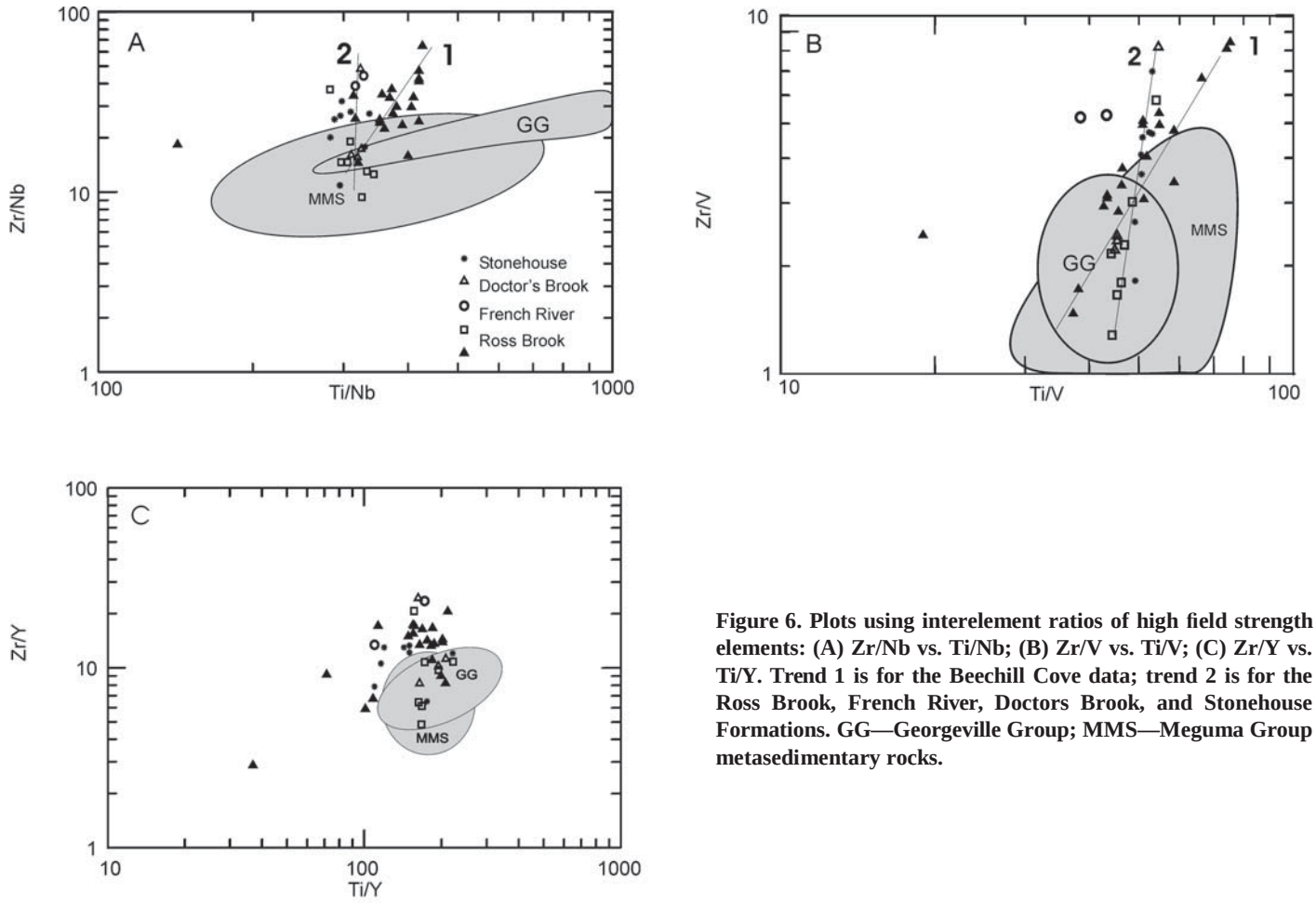

Figure 6. Plots using interelement ratios of high field strength elements: (A) Zr/Nb vs. Ti/Nb; (B) Zr/V vs. Ti/V; (C) Zr/Y vs. Ti/Y. Trend 1 is for the Beechill Cove data; trend 2 is for the Ross Brook, French River, Doctors Brook, and Stonehouse Formations. GG—Georgeville Group; MMS—Meguma Group metasedimentary rocks.

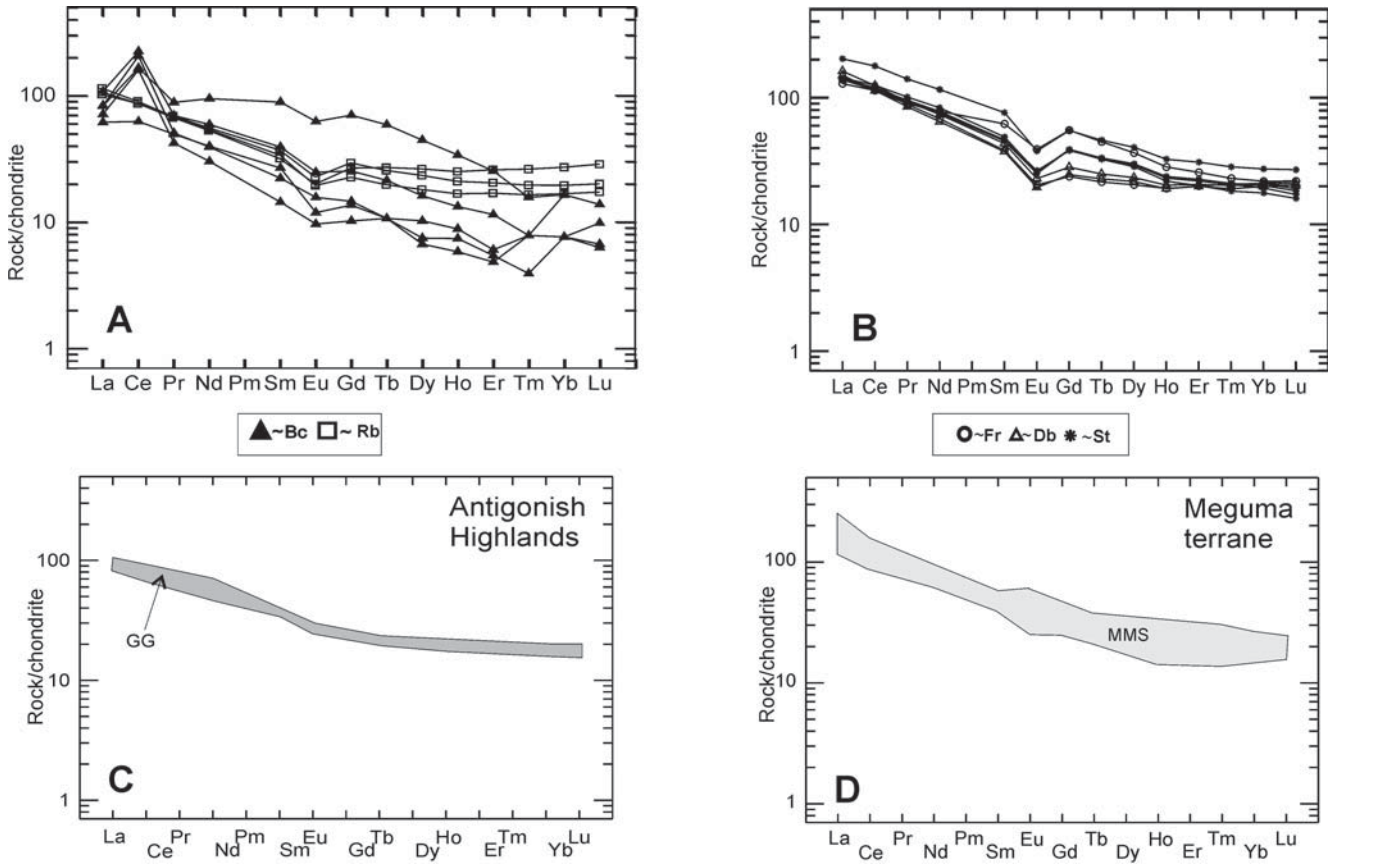

Figure 7. Chondrite-normalized rare earth element (REE) profiles for (A) Beechill Cove (BC) and Ross Brook (Rb) Formations, (B) French River (Fr), Doctors Brook (Db), and Stonehouse (St) Formations compared with REE profiles for (C) the Neoproterozoic turbidites of the Georgeville Group (GG) in the Antigonish Highlands and (D) the Meguma Group metasedimentary rocks (MMS). Normalizing values from Sun and McDonough (1989).

lie on a trend of higher Zr/V with higher Ti/V (trend 1). The Ross Brook, French River, and Stonehouse Formations display a wide range in Zr/V for relatively constant Ti/V ratios, and the data for these formations fall along the same trend line (trend 2).

On the Zr/Y vs. Ti/Y plot (Fig. 6C), the formations are virtually indistinguishable, although the Beechill Cove Formation displays the widest range in both ratios.

Total REEs increase up-section in the Arisaig Group. Chondrite-normalized REE patterns for the Beechill Cove Formation (Fig. 7A) are gently sloping and display moderate LREE (light rare earth element) enrichment (La_n/Sm_n = 1.0–4.8; La_n/Yb_n 5.0–14.5). For RFD rocks (Fig. 7B), although total REEs are higher, normalized elemental ratios show a similar degree of LREE enrichment (La_n/Sm_n of 2.0–4.0; La_n/Yb_n from 4.0 to 9.9). Although Stonehouse rocks also display LREE enrichment, they have a more restricted range (La_n/Sm_n of 2.6–4.1; La_n/Yb_n from 9.5 to 10.1). All formations display a negative Eu anomaly.

Sm-Nd Isotope Data

Fine-grained detrital sediments tend to have a restricted range of Sm/Nd ratio that is likely to represent the weighted average Sm/Nd ratio of their crustal source regions (e.g., Thorogood, 1990). The Nd isotope signature in clastic sedimentary rocks is interpreted to represent the weighted average of values for detrital contributions from the various source areas (see Arndt and Goldstein 1987; Murphy and Nance, 2002), and the range in ε_{Nd} values (Table 2) may be attributed to the isotopic heterogeneities of the source rocks.

The data for RFD and SH samples are listed in Table 2 (see Murphy et al., 1996a, for BC data). To facilitate comparison between formations, ε_{Nd} values (relative to CHUR [chondritic uniform reservoir]) given in the text are for the same depositional age (t = 430 Ma). Taken together, all sedimentary rocks are characterized by strongly negative ε_{Nd} values (Figs. 8A, 8B) and T_{DM} ages that are more than 1.0 b.y. older than the depositional age. In addition, however, there is an overall trend toward increasingly negative ε_{Nd} values from the base to the top of the group. In the Beechill Cove Formation, ε_{Nd} ranges from –4.8 to –6.1. In the RFD samples, ε_{Nd} ranges from –6.0 to –7.9, whereas in samples of the Stonehouse Formation, ε_{Nd} ranges from –7.6 to –9.3 (Fig. 8C).

U-Pb Detrital-Zircon Data

Sample BB-1 (Table 3, Fig. 9) is dominated by late Neoproterozoic zircons (27 analyses) with a cluster from ca. 644 ± 7 Ma to 593 ± 10 Ma (age of the youngest zircon dated in this sample). In the cumulative probability plot, there are peaks at ca. 595 and ca. 615 Ma. Older Neoproterozoic zircons (two analyses) were dated at ca. 677 ± 8 Ma and 748 ± 12 Ma. Of the remaining analyses (Table 3), four zircons are between ca. 1100–1200 Ma and three are between ca. 1500–1700 Ma one is Archean (2.5 Ga).

Sample BC-1 (Table 3, Fig. 10) yielded four early Paleozoic ages: two Ordovician zircons with concordia ages of 448 ± 8 and 464 ± 6 Ma

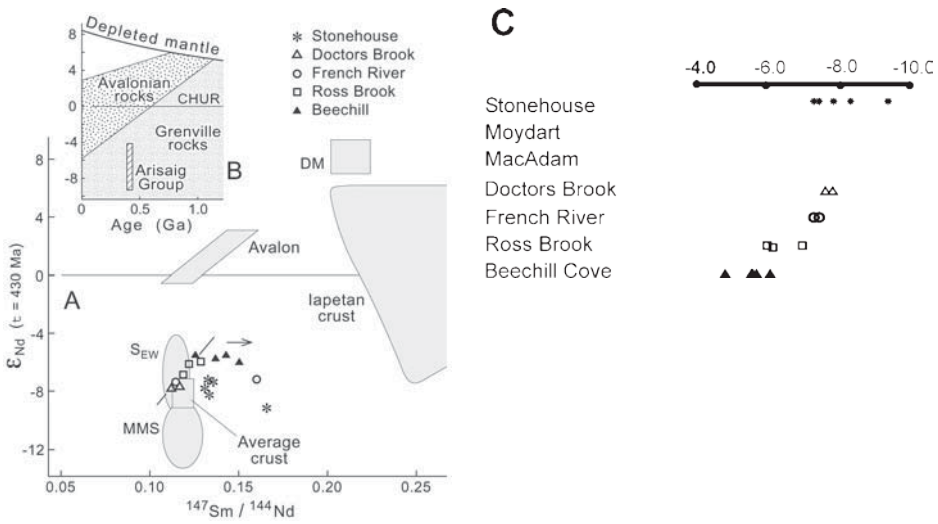

Figure 8. (A) Diagram of $\varepsilon_{Nd(t)}$ vs. $^{147}Sm/^{144}Nd$ (at t = 430 Ma), comparing Sm-Nd isotope data for the Arisaig Group (see Table 2) with typical Sm-Nd isotope compositions of Avalonian crust (Murphy and MacDonald, 1993; Murphy et al., 1996b). The Sm-Nd isotope characteristics for the average upper crust are bracketed between modern global average river sediment ($^{147}Sm/^{144}Nd$ = 0.114; T_{DM} = 1.52 Ga; Goldstein and Jacobsen, 1988) and the average age of sedimentary mass (Miller et al., 1986). See also Thorogood (1990). Iapetan crust includes normal and depleted island-arc tholeiites and ophiolitic complexes in Newfoundland and Norway (MacLachlan and Dunning, 1998; Pedersen and Dunning, 1997). Silurian strata of England and Wales (S_{EW}) from Thorogood et al. (1990) and Meguma terrane metasedimentary rocks (MMS) from Clarke et al. (1997). DM—depleted mantle. (B) $\varepsilon_{Nd(t)}$ vs. time (Ga) diagram (at t = 430 Ma) comparing Sm-Nd isotope data for the Arisaig Group (see Table 3) with typical Sm-Nd isotope compositions of Avalonian crust (Murphy et al., 1996b, 2000). Field for Grenville rocks after Patchett and Ruiz (1989); Dickin and McNutt (1989); Dickin et al. (1990); Daly and McLelland (1991); McLelland et al. (1993); Dickin (2000). CHUR—chondritic uniform reservoir. (C) Variation in $\varepsilon_{Nd(t)}$ (t = 430 Ma) with stratigraphic height in the Arisaig Group. Beechill Cove Formation data from Murphy et al. (1996).

and two Cambrian zircons both with a concordia age of 527 ± 7 Ma. Eight zircons yielded late Neoproterozoic ages between 617 ± 10 and 545 ± 5 Ma; three older Neoproterozoic zircons yielded ages of 699 ± 10, 698 ± 17, and 666 ± 28 Ma. Six zircons yielded Mesoproterozoic ages at 940, 980, 1010, 1030, 1250, and 1260 Ma. One zircon yielded a late Paleoproterozoic age of 1750 Ma, and five zircons yielded a cluster of Paleoproterozoic ages between 2080 and 2180 Ma. One zircon yielded an Archean age of 2710 Ma.

Sample FR-1 (Table 3, Fig. 11) yielded three Paleozoic zircons with ages 444 ± 28, 519 ± 10, and 533 ± 7 Ma. Two zircons yielded ages at the Neoproterozoic/Cambrian boundary (542 ± 6 and 546 ± 8 Ma). Seven zircons yielded Neoproterozoic ages between 560 ± 17 and 755 ± 7 Ma. The number of analyses is insufficient to ascertain the possible existence of discrete clusters within that interval. Seven zircons yielded Mesoproterozoic ages between 910 and 1230 Ma. One zircon yielded an older Mesoproterozoic age of 1570 Ma. Finally, six zircons yielded Paleoproterozoic ages between 1780 and 2080 Ma.

Sample SH-1 (Table 3, Fig. 12) yielded seven Paleozoic zircons. Of these, two have latest Silurian–earliest Devonian ages of 416 ± 6 and 410 ± 6 Ma, three zircons yielded Ordovician ages (ca. 477, 494, and 498 Ma), and two zircons yielded Cambrian ages at 522 and 517 Ma. Five zircons yielded late Neoproterozoic ages between 610 ± 34 and 548 ± 8 Ma. One zircon yielded an older Neoproterozoic age of 834 ± 10 Ma. Nine zircons yielded Mesoproterozoic ages at 1040,

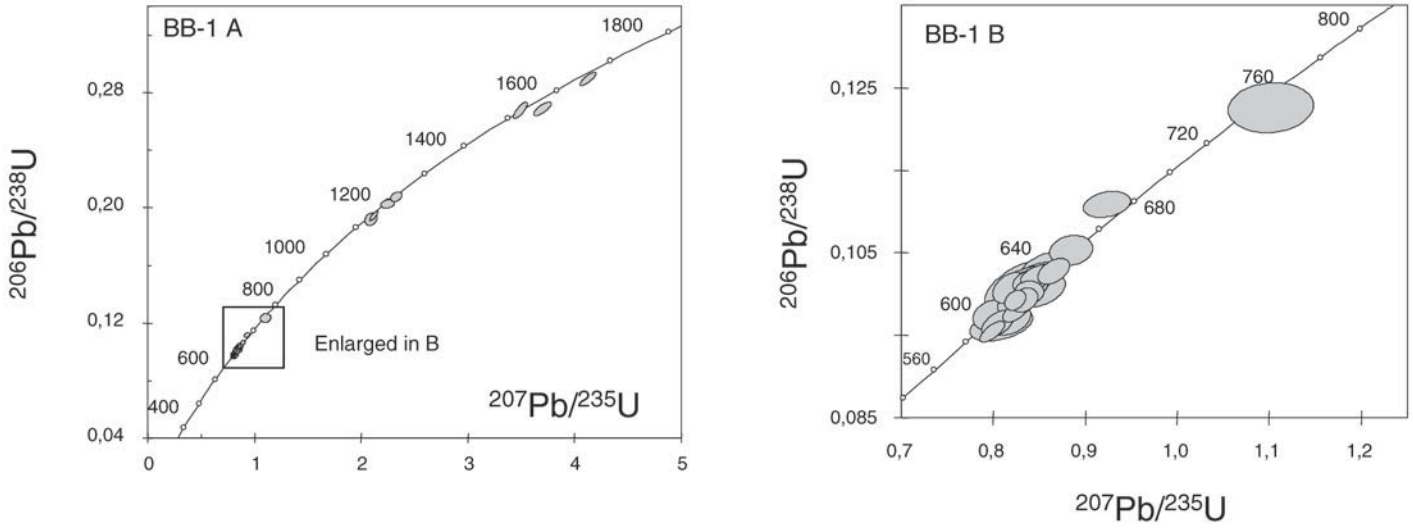

Figure 9. (A) U-Pb concordia plot for all analyses of sample BB-1. (B) Enlargement of concordia plot for Neoproterozoic zircons of sample BB-1. (ellipses are 2σ).

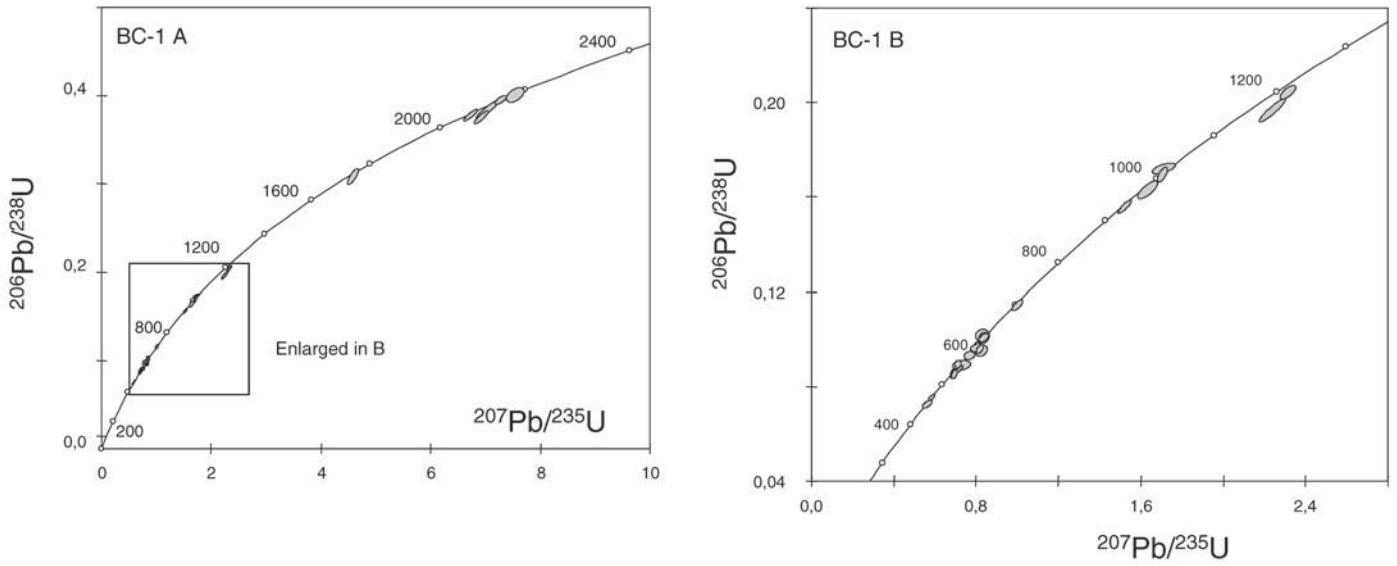

Figure 10. (A) U-Pb concordia plot of sample BC-1. (B) Enlargement of concordia plot for Neoproterozoic–Cambrian zircons of sample BC-1 (ellipses are 2σ).

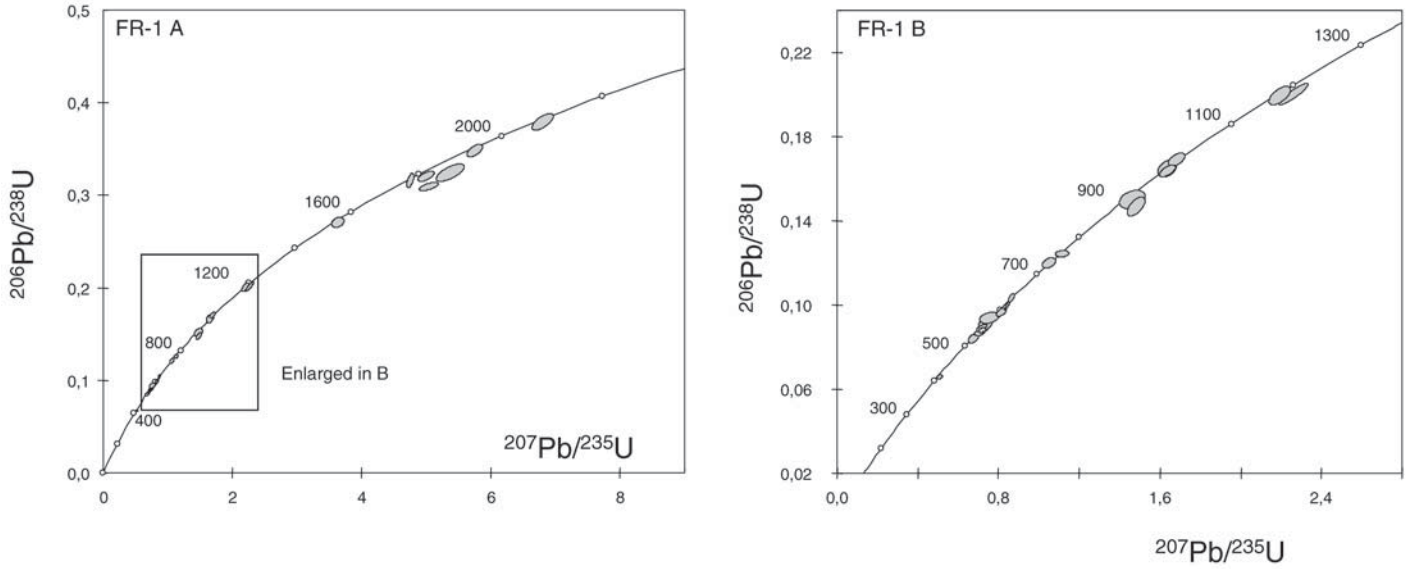

Figure 11. (A) U-Pb concordia plot for all analyses of sample FR-1. (B) Enlargement of concordia plot for Neoproterozoic–Mesoproterozoic zircons of sample FR-1 (ellipses are 2σ).

1160, 1260, 1430, 1480, 1490, 1540, 1600, and 1620 Ma. Three zircons yielded Paleoproterozoic ages at 1930, 2100, and 2120 Ma.

The abundance of pre-Neoproterozoic zircons (as deduced from zircon age clusters) increases from <20% in sample BB-1 to ~50% in samples BC-1, FR-1, and SH-1. Whereas sample BB-1 does not contain Paleoproterozoic zircons, samples BC-1, FR-1, and SH-1 contain a significant proportion (>10%) of Paleoproterozoic zircons. Archean zircons are equally scarce in all samples (Table 3).

INTERPRETATION

Lithogeochemistry and Sm-Nd Isotope Data

The Arisaig Group overlies a typically Avalonian Neoproterozoic to Lower Silurian succession. In order to assess the contribution of underlying Avalonian basement rocks to the geochemistry and isotopic signature of the clastic rocks of the Arisaig Group, representative suites were selected for comparison (Figs. 4–7). These suites are the clastic rocks of the ca. 618–610 Ma Georgeville Group (GG), which are an example of sedimentary rocks derived almost exclusively from erosion of adjacent coeval Avalonian volcanic rocks (Murphy and MacDonald, 1993), the ca. 460 Ma mafic (M) and felsic (F) volcanic

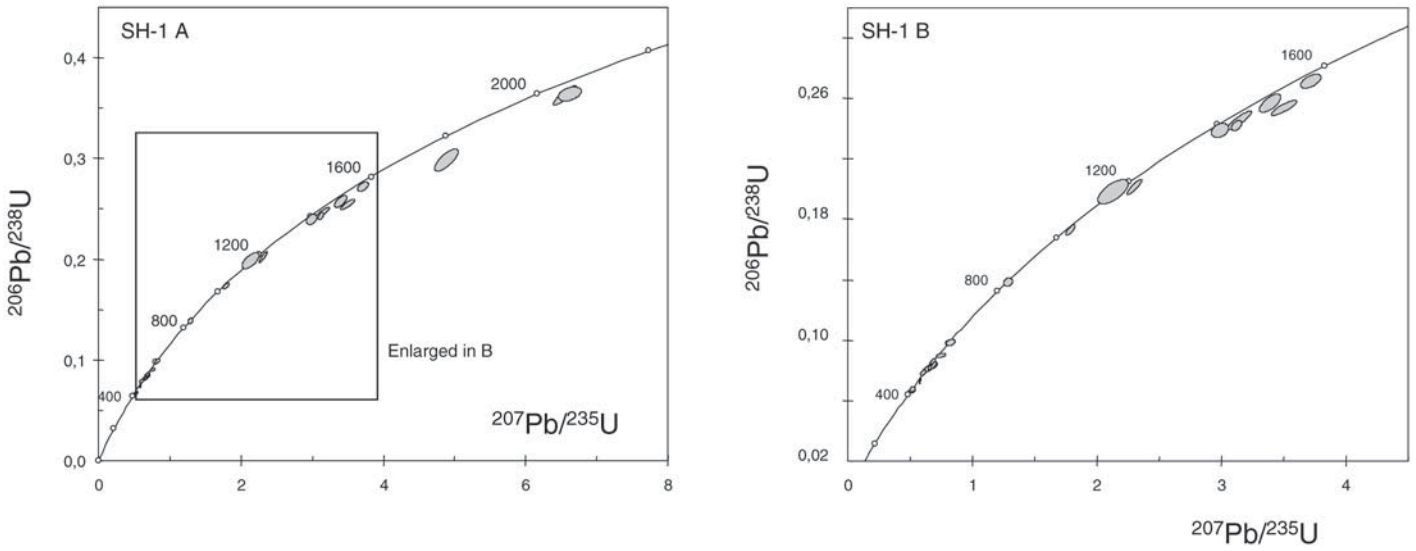

Figure 12. (A) U-Pb concordia plot of sample SH-1. (B) Enlargement of concordia plot for Neoproterozoic–Cambrian zircons of sample SH-1 (ellipses are 2σ).

rocks of the Dunn Point Formation that immediately underlie the Arisaig Group, which also display a typically Avalonian signature (Murphy et al., 1996b), and the Cambrian–Ordovician Meguma Group metasedimentary rocks (MMS), which belong to the Meguma terrane, located immediately to the south of the Avalon terrane in mainland Nova Scotia.

The geochemical and Sm-Nd isotope signatures of the all Arisaig Group rocks show such fundamental geochemical and isotopic differences from both representative suites that a significant chemical contribution from the underlying basement rocks is unlikely. Arisaig Group clastic rocks have lower Fe_2O_3 and MgO and higher SiO_2 contents than Georgeville Group rocks and have K/Rb ratios close to the average for continental crust (Figs. 3–5). The higher Fe_2O_3 and MgO and lower SiO_2 contents and lower K/Rb ratios in Georgeville Group rocks reflect derivation from a more mafic source (Taylor and McLennan 1985). Geochemical contrasts of the Arisaig Group rocks with those of the Georgeville Group and Meguma Group metasedimentary rocks are evident in plots involving interelement ratios of high field strength elements (Fig. 6) and are especially significant because these plots are relatively insensitive to sedimentary processes that affect the modal abundance of the accessory phases in which these elements reside (McLennan et al., 1980). On interelement ratio plots (Fig. 6), when compared to Arisaig Group rocks, the Georgeville Group rocks have a much wider range in Ti/Nb, lower Zr/Nb, and more restricted ranges in Zr/Y and Zr/V ratios. Chondrite-normalized REE patterns (Figs. 7A, 7B) for Arisaig Group rocks are characterized by higher REEs, especially Ce to Tb, and gentler profiles that are similar to modern intracontinental rifts and differ from the arc signatures of the Georgeville Group sedimentary rocks (Fig. 7C; see McLennan et al., 1990; Murphy and MacDonald, 1993). Georgeville Group sedimentary rocks contain higher ε_{Nd} values (ranging from +0.16 to +4.39, calculated for a 615 Ma depositional age) and younger $\varepsilon_{Nd}(T_{DM})$ model ages (1.15–0.96 Ga) that are typical of Avalonian crust (Murphy and MacDonald, 1993; Murphy et al., 1996; Murphy and Nance, 2002).

Similar contrasts between the Arisaig Group and Dunn Point bimodal volcanic rocks are also evident (Fig. 4). In general, Arisaig Group compositions do not lie between the compositions of the volcanic rocks, implying limited contribution from the underlying volcanic rocks. The contrast is especially obvious when comparing Sm-Nd isotope characteristics. In comparison to the Arisaig Group, Dunn Point volcanic rocks have higher ε_{Nd} values (ur, uniform reservoir) (ranging from –0.10 to + 5.07, at 430 Ma), and lower $\varepsilon_{Nd}(T_{DM})$ model ages (1.05–0.88 Ga, Murphy et al. 1996b).

The Sm-Nd isotope data broadly constrain potential sources for the detritus (Fig. 8A). For example, the linear correlation between $^{147}Sm/^{144}Nd$ and ε_{Nd} in the Ross Brook and Doctors Brook samples is consistent with derivation from the same crustal province. Most samples along this trend lie above the average crustal value, suggesting a minor contribution from a more juvenile source, possibly the underlying Avalonian rocks. Although one French River and one Beechill Cove sample lie on the same trend, other Arisaig Group samples with similar ε_{Nd} values have variable $^{147}Sm/^{144}Nd$ ratios, suggesting the additional influence of a different crustal province. This distinction is especially marked for Stonehouse Formation samples. The identity of this province, however, cannot be uniquely determined from these data. Potential sources such as coeval Silurian strata in England and Wales (S_{EW} in Fig. 8A) or the Meguma Group metasedimentary rocks (MMS in Fig. 8A) cannot have supplied detritus of the appropriate composition. Iapetan complexes, which were accreted to the Laurentian margin during the Ordovician, are highly diverse in composition and include ophiolites, boninites, and island-arc complexes. This diversity is reflected in their variable Sm-Nd isotope compositions, and although they are a possible source, the extent of their contribution to the detritus is difficult to assess.

Detrital-Zircon Data

The detrital-zircon populations in the continental Bears Brook Formation are remarkably similar to those in the underlying Cambrian rocks (sample HMB-1; Murphy et al., 2004) in the Antigonish Highlands, which are overwhelmingly dominated by Neoproterozoic zircons (56 in a total of 62), including a cluster from ca. 580 Ma to 680 Ma. Less pronounced older Neoproterozoic clusters feature three concordant analyses at 715–707 Ma and three discordant analyses with $^{207}Pb/^{206}Pb$ ages ranging from 764 to 756 Ma. There are five Mesoproterozoic zircons (ca. 1023, 1154, 1218, 1542, and 1608 Ma), and one is Paleoproterozoic

(1938 Ma). These zircons are thought to have been derived from the underlying Avalonian basement (Murphy et al., 2004). The detrital-zircon population in sample HMB-1 is remarkably similar to the population of sample BB-1 (Figs. 9 and 13), a fact that strongly suggests that BB-1 was primarily derived from erosion of underlying Avalonian basement. This interpretation is consistent with paleocontinental reconstructions that place Avalonia as a microcontinent at 460 Ma, ~20° north of Gondwana and 10° south of Laurentia (e.g., Torsvik et al., 1996; Fortey and Cocks, 2003), that was isolated from non-Avalonian sources.

The clastic rocks of the Arisaig Group contain a much wider range of detrital-zircon populations than BB-1. Samples BC-1, FR-1, and SH-1 all contain Ordovician–Silurian zircons. Some of these zircons are similar to the depositional age of the respective strata. The ca. 460 Ma zircon in BC-1 is most reasonably derived from the underlying Dunn Point volcanic rocks. The ca. 440 Ma zircon data suggest that the predominantly siliciclastic Arisaig Group was deposited in a volcanically active regional tectonic environment. Chandler et al. (1987) pointed out that ca. 440 Ma magmatism is common in Avalonia (see Greenough et al., 1993), in terranes accreted to Laurentia to the north of Avalonia and in the Meguma terrane to the south of Avalonia (see also Keppie et al., 1998). Middle to Late Silurian magmatism is also common in the Northern Appalachians (van Staal et al., 1998) including in northern Cape Breton (Keppie et al., 1992), in the Tobique belt of New Brunswick (Dostal et al., 1989), and in coastal Maine (Osberg et al., 1985). Bergström et al. (1997) pointed out that K-bentonite ash beds of Llandoverian and Ludlovian age that occur in the Arisaig Group are related to regionally extensive volcanism in the Appalachian-Caledonide belt. Although it is possible that some of the Silurian zircons could have been derived from erosion of a Silurian volcanic belt, it is also possible that some zircons may have been originally transported as airborne ash and subsequently reworked from coeval K-bentonite beds within the Arisaig Group.

Interpretation of the tectonic significance of Cambrian and Proterozoic zircon populations in the Arisaig Group clastic rocks is constrained by the whole-rock geochemistry and Sm-Nd isotope signature, which indicate that these rocks were predominantly derived from non-Avalonian crust. The very low ε_{Nd} values imply that most of the sediment was derived either directly or indirectly from more ancient basement sources. A comparison between the U-Pb detrital-zircon ages of the Arisaig Group and the age of tectonothermal events in potential source areas is shown in Figure 14. Most potential source regions are characterized by late Neoproterozoic to Early Cambrian tectonothermal activity, and so are potential sources for the zircons in this age range. Although some of these zircons could have been derived from the underlying Avalonian basement, the Sm-Nd data indicate that such a contribution is probably minor. Eastern Laurentia, Baltica, and Amazonia are potential sources for ca. 2.1–0.9 Ga zircons. The West Africa craton is characterized by the absence of tectonothermal events between 2.0 and 0.65 Ga (e.g., Rocci et al., 1991) and so cannot have been a source of these zircons. Similarly, as the Meguma terrane metasedimentary rocks of late Neoproterozoic–Early Ordovician age contain zircons derived from the West African craton (Krogh and Keppie, 1990), the Meguma terrane is also an unlikely source. In addition, these underwent greenschist- to amphibolite-facies metamorphism during Arisaig Group deposition, implying they were not at the surface during Arisaig Group deposition and so could not have provided a source for the Arisaig Group detritus.

Amazonia and Baltica both had tectonothermal events at times (e.g., Texiera et al., 1989; Gower et al., 1990) that indicate that these cratons could have been a source of the zircons in the Arisaig Group sedimentary rocks. However, there is a wealth of paleomagnetic and paleontological data that indicates that Avalonia had separated from Amazonia by the Early Ordovician and by the end of the Ordovician was ~2000 km north of the Gondwanan margin (Fig. 15, Cocks and Torsvik, 2002; Fortey and Cocks, 2003; Hamilton and Murphy, 2004). Thus direct derivation from Amazonia is unlikely. Although Neoproterozoic Avalonian clastic rocks were derived from Amazonia (e.g., Krogh and Keppie, 1990; Nance and Murphy, 1994, 1996; Keppie et al., 1998), these rocks (e.g., the Georgeville Group) have very different Sm-Nd isotope signatures (Murphy and MacDonald, 1993), negating the possibility that significant amounts of Amazonian zircons are recycled from Avalonian sedimentary rocks into Arisaig detritus.

Ordovician–Silurian paleocontinental reconstructions (Fig. 15) based on paleomagnetic and faunal data (e.g., Cocks and Torsvik, 2002; Fortey and Cocks, 2003) show Avalonia adjacent to Baltica by the time of deposition of the Beechill Cove Formation, at ca. 440 Ma, although the nature of the collision between Baltica and Avalonia is controversial (e.g., Soper and Woodcock, 1990; Pickering et al., 1988). Baltica could have provided the bulk of the zircons deposited in the Beechill Cove sample. This interpretation is compatible with the paleocurrent data in the Arisaig Group,

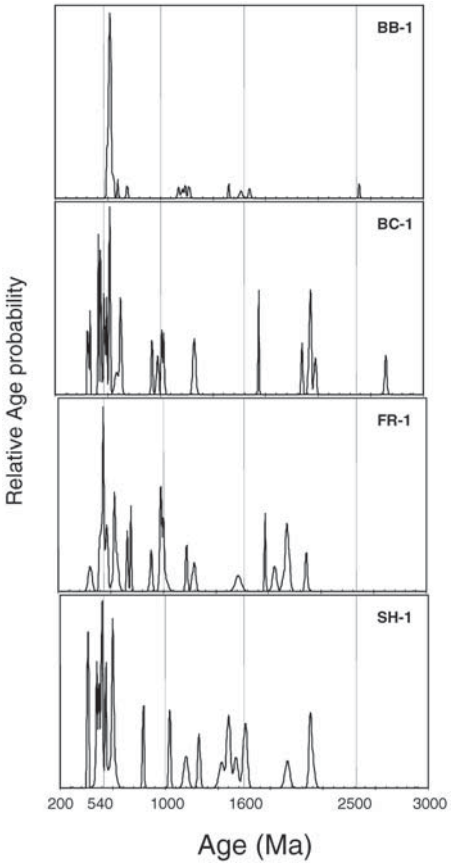

Figure 13. Relative age probability plots of zircons in (top to bottom) BB-1, BC-1, FR-1, and SH-1 (ages and 2σ errors used are those labeled "reported age" in Table 3).

which show derivation from the northeast (present coordinates).

By the time of deposition of the ca. 425 Ma French River and ca. 400 Ma Stonehouse Formation in the Early Devonian, Avalonia-Baltica had collided with the eastern Laurentian margin, resulting in complex deformation and uplift of the Laurentia-Baltica margin and of terranes inboard of Avalonia (e.g., the Gander terrane, van Staal et al., 1990, 1998). Such deformation would account for the Late Silurian (ca. 415 Ma) loading of the Avalonian margin documented by Waldron et al. (1996), and the uplift would expose older basement, which we speculate was the source of the more negative ε_{Nd} values and variable $^{147}Sm/^{144}Nd$ ratios in Stonehouse Formation rocks. If so, the Late Silurian depositional setting may have been a foreland basin associated with Avalonian–Laurentian convergence.

According to van Staal et al. (1996, 2003), U-Pb detrital and xenocrystic zircon studies in lower Paleozoic Gander terrane rocks indicate

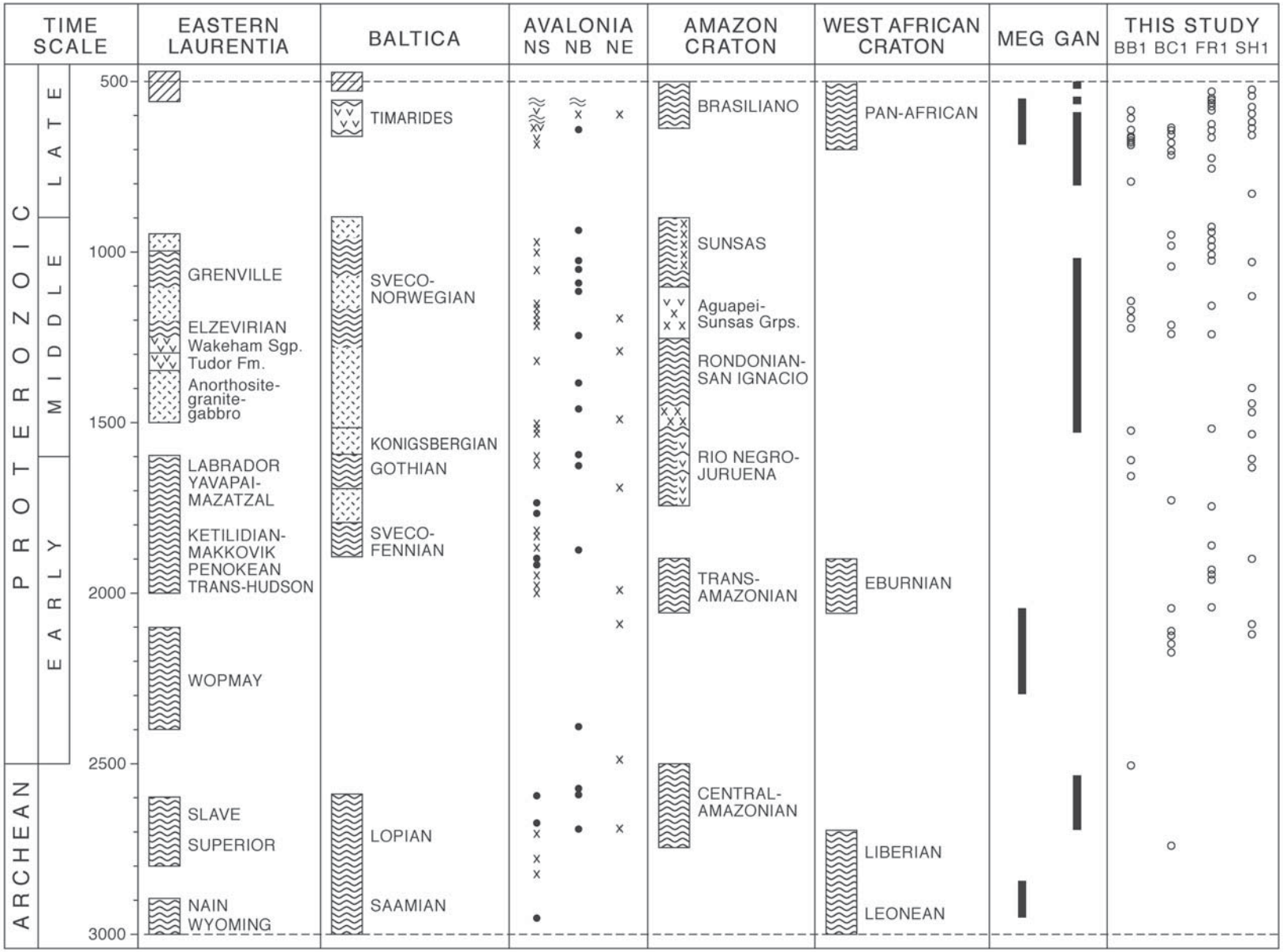

Figure 14. Comparison of detrital-zircon ages from Bears Brook Formation and Arisaig Group rocks with those from the Meguma terrane (Krogh and Keppie, 1990) and Avalonia (Nova Scotia—NS, Keppie et al., 1998; New Brunswick—NB, Bevier et al., 1990; New England—NE, Karabinos and Gromet, 1993). Ages: x—concordant U-Pb zircon ages; filled circles—discordant $^{207}Pb/^{206}Pb$ ages. Also shown are tectonothermal events in Baltica (Gower et al., 1990; Goodwin, 1991; Starmer, 1993; Roberts and Siedlecka, 2002; Roberts, 2003), eastern Laurentia (Hoffman, 1989; Connelly and Heaman, 1993; McLelland et al., 1993; Martignole et al., 1994; Gower and Tucker, 1994; Cawood et al., 2001), the Amazon craton (Texiera et al., 1989; Sadowski and Bettencourt, 1996; and references therein), northwest Africa (Rocci et al., 1991), Meguma terrane (MEG) (Krogh and Keppie, 1990), and Gander terrane (GAN) (van Staal et al., 1996, 2003). Boxes with waves denote periods of orogenesis; boxes with diagonal lines are important periods of rifting.

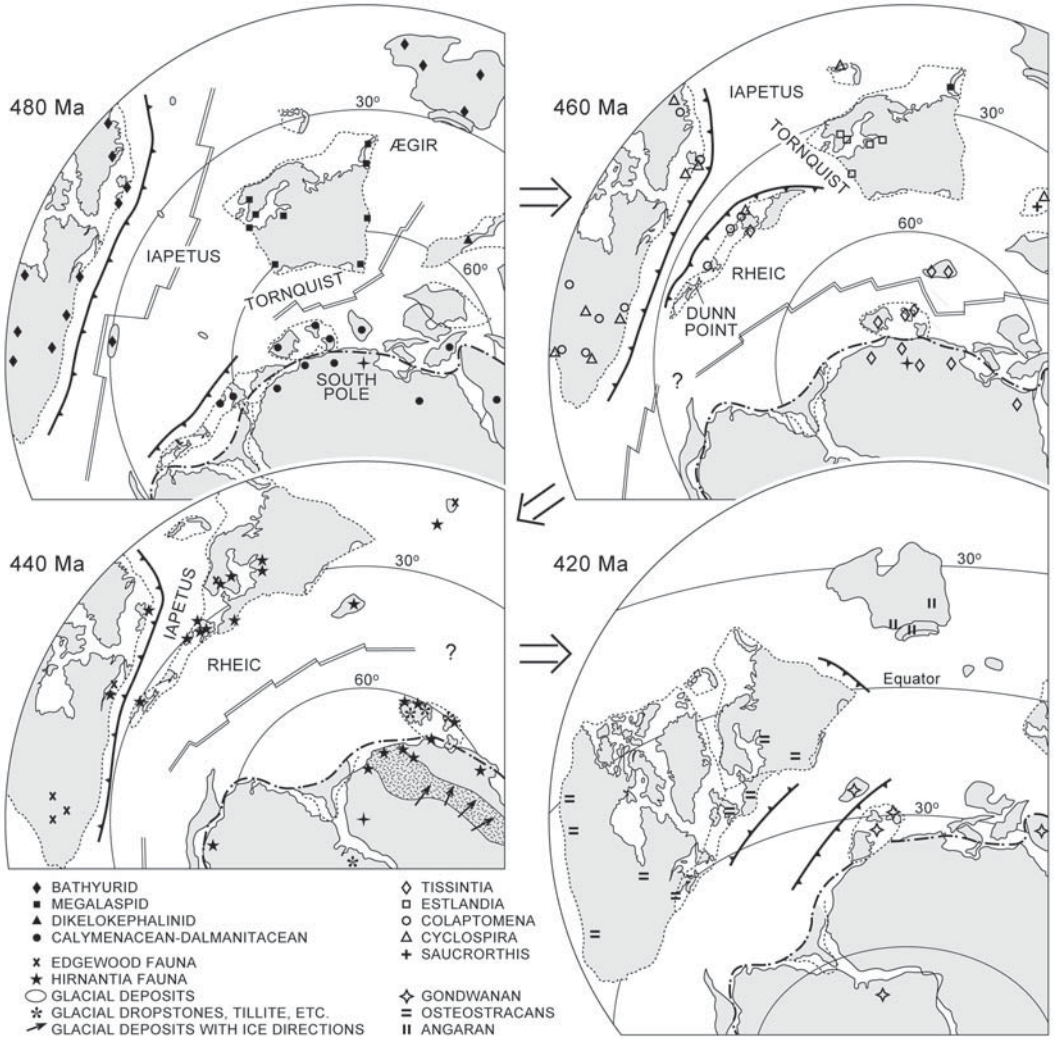

Figure 15. Early Ordovician to Late Silurian paleogeographic reconstructions of the circum-Atlantic region (based on Cocks and Torsvik, 2002; Fortey and Cocks, 2003).

that this terrane has a basement consisting of latest Neoproterozoic–Cambrian (0.55–0.51 Ga), Neoproterozoic (0.8–0.6 Ga), Mesoproterozoic (1.55–1.0 Ga), and Archean (2.9–2.5 Ga) rocks. If so, the Gander terrane could provide a source, although the abundance of Arisaig Group detrital zircons with ages between 2.2 and 1.5 Ga suggests that it was not the dominant source. A Laurentian source, on the other hand, for Arisaig Group detrital zircons would account for the diminished relative abundance of Neoproterozoic zircons and would provide a source for the 2.2–1.5 Ga zircons. For example, FR-1 samples are characterized by an absence of zircons between 570 and 530 Ma. The latest Neoproterozoic and Cambrian zircons present in these samples may be derived from the rift-related igneous rocks formed along the Laurentia-Baltica margin during the opening of the Iapetus Ocean.

According to Boucot et al. (1974), paleocurrent directions in the uppermost Stonehouse Formation are from the southwest. The only potential source terrane known outboard of Avalonia is the Meguma terrane. However, in addition to the lithogeochemical and Sm-Nd isotope data, general geological considerations indicate that the Meguma terrane is unlikely to have been the source of the Arisaig Group sediments because this terrane underwent metamorphism between 415 and 390 Ma and was intruded by batholiths at 370 Ma (e.g., Clarke et al., 1993, 1997; Keppie and Dallmeyer, 1995). The earliest evidence of exhumation of Meguma terrane rocks is their occurrence as clasts in uppermost Devonian–Tournaisean Horton Group rocks (e.g., Jennex et al., 2000; Murphy, 2000; Murphy and Hamilton, 2000). The relationship between the geochemical and isotopic data and the paleocurrent data remains enigmatic.

SYNTHESIS

Deposition of the Silurian–Lower Devonian Arisaig Group spanned important accretionary events in the Appalachian orogen. The strata are unmetamorphosed and were not deformed until the Middle Devonian, and deposition of the Arisaig Group, therefore, is interpreted to have occurred along the trailing edge of Avalonia during terrane accretion. Nevertheless, the geochemistry and isotopic signature of these rocks clearly record the signature of these regional tectonic events. Prior to the deposition of the Arisaig Group, detrital zircons that were derived from Avalonian basement were deposited in what is now the Bears Brook Formation, consistent with Avalonia's paleogeographic position as a New Zealand–style microcontinent at ca. 460 Ma. Taken together, the geochemical and Sm-Nd and U-Pb isotope characteristics of the Arisaig Group are inconsistent with derivation from Avalonian basement and indicate an important component of ancient crust in the source regions. Comparison of detrital-zircon populations with known tectonothermal events in potential source regions suggests proximity of Eastern Avalonia

to Baltica in the latest Ordovician and to Laurentia by the Middle Silurian; such locations are consistent with paleogeographic maps based on faunal and paleomagnetic data (e.g., Cocks and Torsvik, 2002; Fortey and Cocks, 2003) and with recent tectonic models for the Appalachian-Caledonide belt (van Staal et al., 1998).

The timing of accretion of Avalonia to Baltica and Laurentia can be confidently constrained by identifying sedimentary sequences that overstep the terrane boundary. The Silurian position of Western Avalonia lies within the range of detritus shed from coeval orogenic events that affected Baltica and Laurentia.

APPENDIX: ANALYTICAL METHODS

U-Pb Analyses

Samples BB-1, BC-1, FR-1, and SH-1 were crushed with a jaw crusher and pulverized with a disc mill. Zircons were separated at the Complutense University of Madrid by heavy-fraction enrichment on a Wilfley table followed by density separation using di-iodomethane (CH_2I_2) and magnetic separation in a Frantz isodynamic separator. Zircons were selected from the least magnetic fraction and hand-picked in alcohol under a binocular microscope. Zircon grains representing all sizes and morphological types present in each sample were selected for LA-ICP-MS analyses. Grains were set in synthetic resin mounts, polished to approximately half their thickness and cleaned in a warm HNO_3 ultrasonic bath. LA-ICP-MS analyses were performed at the Natural History Museum, London. Analytical instrumentation consisted of a UP213 frequency-quintupled Nd:YAG-based laser-ablation system (NewWave Research, Fremont, USA) coupled to a (Thermo Elemental) PQ3, quadrupole-based ICP-MS instrument with enhanced sensitivity (S-Option) interface. Instrument, operating parameters, and procedures used for individual zircon analyses were as given in Jeffries et al. (2003).

Samples and standard were ablated in an air-tight sample chamber flushed with helium for sample transport. The laser was focused on the sample surface, and energy density was kept constant for each analysis. The samples were rastered along lines ~25–50 μm long (depending on zircon size), and a constant raster speed was used for each analysis. Nominal beam diameter was 30 μm for zircon analyses of samples BB-1, but all zircons from samples BC-1, FR-1, and SH-1 were very small (typically 20–40 × 50–75 μm in section), and a nominal beam diameter of 18 μm was used for these three samples. It should be noted here that in spite of the relatively small volume of sample ablated with an 18 μm spot size, the short line rasters, and the short collection times, the precision of analyses compares well with that of other studies in which nominal beam diameters of 45–80 μm were used (e.g., Fernández-Suárez et al., 2002). Data were collected in discrete runs of 20 analyses, comprising 12 unknowns bracketed before and after by 4 analyses of the standard zircon 91500 (Wiedenbeck et al., 1995). During the analytical sessions of samples BB-1, BC-1, FR-1, and SH-1 the standard 91500 yielded a weighted average (n = 96) of 1062.2 ± 1.2 Ma (MSWD [mean square of weighted deviates] = 1.06) for the $^{206}Pb/^{238}U$ age (certified ID-TIMS [isotope dilution–thermal-ionization mass spectrometry] $^{206}Pb/^{238}U$ age: 1062.4 ± 0.4 Ma) and a weighted average of 1064.6 ± 1.7 Ma (MSWD = 0.6) for the $^{207}Pb/^{206}Pb$ age (certified ID-TIMS $^{207}Pb/^{206}Pb$ age: 1065.4 ± 0.3 Ma).

Data for sample zircons were collected for up to 150 s per analysis with a gas background taken during the initial ~60 s. For each analysis, time-resolved signals were obtained and then carefully studied to ensure that stable flat signal intervals (free from inclusions, core-rim features, zones of high common Pb, or evidence of fractionation) were used in the age calculations. Preliminary selection of background and analysis signal intensities and data calculation were performed by using LAMTRACE, a macro-based spreadsheet written by Simon Jackson, Macquarie University, Australia. Background- and mass-bias–corrected signal intensities and counting statistics were calculated for each isotope. Concordia age calculations were performed and concordia and cumulative probability plots were created through the use of Isoplot/Ex rev. 2.49 (Ludwig, 2001). Data treatment, assignment of final ages, and errors for individual analyses, estimation of common Pb, and criteria for rejection of analyses are those detailed in Fernández-Suárez et al. (2002) and Jeffries et al. (2003).

Common Lead

The ages reported in Table 3 have not been corrected for common Pb as ^{204}Pb measurements are rendered useless by the isobaric interference from Hg, a contaminant present in the Ar supply gas. ^{204}Hg interferes on ^{204}Pb, and the ^{202}Hg peak is too small to allow a reliable overlap correction of acceptable precision. The ^{208}Pb correction method (Compston et al., 1984; Ludwig, 2001) cannot be applied reliably to U-Pb analyses as the assumption of concordance between the radiogenic $^{206}Pb/^{238}U$ and $^{208}Pb/^{232}Th$ ratios is not always justified. This difficulty is particularly obvious in U-Pb dating of detrital-zircon populations in which only one analysis per grain is obtained and extrapolations on the behavior of the U-Th-Pb system cannot be applied as, for instance, in the case of U-Th-Pb dating of cogenetic magmatic zircons.

Andersen (2002) has proposed a common-Pb correction method that neither uses ^{204}Pb nor assumes concordance, but relies instead on the assumption of coherent behavior of the U-Pb and Th-Pb systems during Pb loss. Application of this correction algorithm revealed significant common-Pb content (i.e., age correction outside analytical error) in eight discordant analyses. These analyses have been rejected and are not reported in Table 3. Prior to such rejection, examination of the time-integrated U-Pb, Th-Pb, and Pb-Pb isotope ratio plots allows the analyst to detect analyses (or parts of an analysis) that contain significant amounts of common lead (e.g., Fernández-Suárez et al., 2002; Jeffries et al., 2003), and the corresponding segments of the signal are not used in the age calculation. Therefore, we are confident that the effect of common Pb in the ages reported in Table 3 is well below total analytical uncertainty and has no influence at all in any of the conclusions derived from the ages reported.

Sm-Nd Analyses

Approximately 0.1 g of rock power was dissolved in Savillex vials by using a mixture of concentrated HF + HNO_3 acids. A mixed ^{150}Nd and ^{149}Sm spike having a known isotope ratio was added to each sample prior to acid digestion. After 5 days of digestion, the solution was evaporated to dryness and then taken up in 6*N* HCl acid for two days. The solution was then dried and taken up in 2.5*N* HCl and loaded on cationic-exchange chromatography columns using AG50W-X8 resin. The REE fraction was then purified, and Sm and Nd were isolated by using a secondary column loaded with Eichrom Ln resin. All reagents were distillate in order to insure a low contamination level. The measured total chemical blanks ranged between 40 and 90 pg.

Sm and Nd contents and Nd isotope composition were analyzed by using a multicollector Finnigan MAT 262 mass spectrometer in static mode. Nd isotope ratios were normalized to $^{146}Nd/^{144}Nd = 0.7219$. The reported values were adjusted to La Jolla Nd standard ($^{143}Nd/^{144}Nd = 0.511860$). During the course of data acquisition, replicates of the standard gave a mean value of $^{143}Nd/^{144}Nd = 0.511888 \pm 0.000016$ (2σ m, n = 12). The in-run precisions on Nd isotope ratios are given at the 95% confidence level. Errors on Nd isotope compositions are <0.002%, and errors on the $^{147}Sm/^{144}Nd$ ratio are estimated to be <0.1%. The ε_{Nd} values were calculated by using $^{147}Sm/^{144}Nd = 0.1967$ and $^{143}Nd/^{144}Nd = 0.512638$ values for the present-day chondritic uniform reservoir (CHUR). The ^{147}Sm decay constant is 6.54×10^{-12} yr^{-1} (Steiger and Jäger, 1977). The T_{DM} values were calculated with respect to both (1) a depleted mantle (DM) having an $\varepsilon_{Nd(t=0)}$ value of +10, isolated from the CHUR since 4.55 Ga, and following a linear evolution and (2) the DePaolo mantle model (DePaolo, 1981, 1988).

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